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THE USE OF THE ULTRAVIOLET IN ANALYTICAL CHEMISTRY

2. QUALITATIVE MICROCHEMICAL ANALYSIS IN THE ULTRAVIOLET

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In microcrystalloscopic analysis, the form or color of the crystals formed by a particular ion on precipitation from a solution by a specific reagent is used as a means of detecting the ion. In some cases the formation of a precipitate can be taken as proof of the presence of the ion. Very few substances possess an observable color, particularly if the crystals are small. It should be noted that linking a colored ion with a definite cation or a colored cation with a definite anion does not solve the problem, since the given colored anion or cation can give colored compounds with other ions. Therefore conclusions as to the presence or absence of some particular ion can only be made on the basis of the crystal form of the precipitate formed. Crystal form however is by no means a certain criterion; the same compound can exist in different crystal forms depending on minor variations in the precipitating conditions, apart from the possibility of co-precipitation with other compounds; many compounds in general give precipitates with such small crystals that even with strong magnification they appear amorphous and their detection by microcrystalloscopic analysis is rendered difficult.

In cases where the substance to be analyzed is of a complex composition and includes several colored compounds, or when both the ions which compose the compound are colored the observed color is not equal to the sum of the colors of the components. In such cases it is necessary either to remove the interfering colored ion or to convert it into a colorless form (e.g. by conversion into a complex compound).

The new ultraviolet microscopy and particularly observation in ultraviolet light using the method of "color transformation" developed by Broomberg [1] has greatly extended the possibilities and scope of solving the above problems.

This method consists briefly in the substitution of the ultraviolet rays in the invisible image given by the objective of the ultraviolet microscope, by visible rays of different colors. In this way colored images of colorless objects are formed, the conditional colors of which are determined not by the normal visual spectrum but by the ultraviolet absorption spectra of the compound under examination.

As a result of the tinging of the ultraviolet absorption by the test compound a characteristic "ultraviolet" color is developed. For its detection a composite beam of light composed of red and ultraviolet rays is used. On projecting such a beam of light on to a fluorescent screen, the fluorescence of which is excited by ultraviolet of a definite wave length,

all the details of the test compound, which is located in the path of the beam and which absorbs ultraviolet rays, will assume different degrees of coloring according to the extent of absorption of the ultraviolet rays by the test compound.

In consequence of this the observer sees a shaded spot surrounded by the light of the fluorescent screen at those places where the rays not absorbed by the test compound have fallen. The shaded spot itself on the screen is colored red by the remaining rays.

The fluorescent screen is chosen so that it emits a white fluorescence under the action of ultraviolet light. This enables one to see the shadow of the test compound more clearly.

The color transformation method has two basic variants.

1) A photographic one, in which three photographs are taken in the ultraviolet for a chosen wave length and colored three different colors - red, green, and blue; the superimposed images of these photographs are simultaneously examined by means of a special apparatus - the chromoscope.

2) A visual one which is based on obtaining colored images on multi-colored fluorescent screens by means of ultraviolet light as described above.

It is possible therefore by means of the ultraviolet microscope to see colored crystals, which absorb ultraviolet light, even when they are completely transparent and colorless in visible light. Crystals which have different ultraviolet absorption spectra will accordingly have a different "ultraviolet" color in the field of vision of the microscope, by means of which they can be identified.

The use of the ultraviolet part of the spectrum for observation can essentially increase the number of microchemical reactions, since the strongest absorption spectral bands of many chemical compounds are located in this region of the spectrum. When observations are made in the ultraviolet it is often possible to use the absorption of a simple compound (and not the complicated compound absorption which it is usually necessary to obtain during microchemical analysis in the visible spectrum) and the analyst's problem reduces to a separation of ions from solution which have the same absorption (i.e. with the same ultraviolet color) as the test compound.

Thus for microchemical determination in the ultraviolet it is not the form of the crystals but their color which plays the chief role. The color can be used even in cases of "hidden" crystalline precipitates.

In the present article it is not our intention to replace microcrystalloscopic analysis in the visible part of the spectra by analysis in the ultraviolet. On the contrary in our view ultraviolet reactions may be regarded only as a useful supplement and for replacing those reactions in the visible spectrum which are inferior with regard to sensitivity and simplicity of detection in complex mixtures etc., i.e., our intention is to pursue the aim of constructing a relatively simple system of microchemical analysis, based on a combination of the usual reactions observed in visible light and in the ultraviolet, and certain luminescence reactions based on the observation of the luminescence of reaction products.

All three types of reaction are easily reproduced by means of the same universal apparatus - the ultraviolet microscope [2].

Apart from the two variants of the color transformation method described above it is possible to use a spectral method for the determination of the

nature of microcrystals by photographing their absorption spectra. By using a specially contructed spectral fitting for the ultraviolet microscope it is possible to get a microphotograph of the test compound together with the image of the spectrograph aperture and the spectrum lines on one photographic plate. Examples of such photographs are given in Fig.1[1]. The mercury spectrum is included as a wave length scale. In this way it is possible to estimate the admission boundary of the crystals under test.

The spectrograms of crystals of $PbCl_2$ and $PbBr_2$ shown on Fig.1 show that crystals of these salts can be confidently distinguished from one another by their absorption spectra. If however substances are present in solution which have similar absorption spectra to those of the test material, it is necessary to perform a preliminary separation in order to avoid erroneous conclusions. The permitted amount of contaminant depends on the ratio of the ultraviolet absorption coefficients of the test sample and the contaminants.

Of the methods considered above, the most suitable one for carrying out large numbers of microchemical analyses is the visual method.

A PRK mercury lamp was used as the light source. An UFS-1 light filter which only transmits infra red and ultraviolet with wave length from 400-250 mμ was fitted on the microsccpe. The fluorescent screen had two layers, one of which was excited only by rays of wave length 365 mμ and has a blue colored fluorescence, while the other was excited by rays of wave length 313 mμ and fluoresced with a green color. As a result of mixing the direct red rays of the light source with green and blue from the screen, the microscope field was of a white color. Crystals which absorb the ultraviolet at $\lambda = 365$ mμ when placed in the field of vision were colored a purple-red color, while those absorbing $\lambda = 313$ mμ had a purple color and those absorbing at $\lambda = 254$ mμ were red. Thus the problem reduces to a selection of chemical reactions in which the reaction products absorb light of some definite wave length, i.e. to obtain for a particular reagent in a given mixture of substances, a characteristic ultraviolet "color" only for the chemical compound which it is necessary to determine. Consequently the absorption coefficients of the reaction products for the substances sought should be high in the wave length region of 365 and 313 mμ.

In spite of its simplicity and color sensitivity the visual method has one drawback, viz., it is impossible to distinguish by this method substances with close absorption limits. In such cases it is better to use the spectrographic method and the method of color photography, which permit a wide variation if necessary in the photographic conditions. These methods can be used when a more detailed study of the absorption spectra of microscopically small amounts of material is necessary.

Reactions for the detection of several cations either on their own or in the presence of each other which can be carried out using the visual method are considered below.

Identification of Alkali Metals. In order to identify the alkali metals we finally decided after a preliminary examination of many compounds to use ammonium hexachloroplatinate, ammonium cobaltinitrite, and potassium trithiosulphatobismuthate as possessing the highest absorption coefficients in the region $\lambda = 365$ mμ.

Reaction for Ammonium. For the detection of ammonium the characteristic absorption of the hexachloroplatinate and cobaltinitrite in the region $\lambda = 365$ mμ was used.

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[1]) See Plate, page 291.

In view of the fact that the corresponding compounds of sodium and potassium also exhibit strong absorption in this region of the ultraviolet, the determination of ammonia was carried out in a gas microcell.

a) As Hexachloroplatinate. A drop of test solution (NH_4Cl) was mixed in a gas cell with a drop of 20% NaOH. The top of the cell was closed with a quartz plate, on the inside face of which a drop of chloroplatinic acid was placed. The cell was gently heated on a microburner. Crystals of ammonium hexachloroplatinate appear instantly on the drop of chloroplatinic acid. These crystals on examination under the microscope are colored an intense red color because of the strong absorption in the ultraviolet.

This reaction is used in microcrystalloscopic analysis in the visible spectrum [3] with a fairly high sensitivity, but the presence of strong absorption in the ultraviolet enables the sensitivity to be increased considerably, as can be seen from a comparison of the results which we obtained for this reaction and those given in the literature for the same reaction in the visible spectrum.

Visible Spectrum		Ultraviolet Spectrum	
Limit of Identification	Limiting Concentration	Limit of Identification	Limiting Concentration
0.1 μg	1:10000	0.042 μg	1:24000

The presence of other cations in the solution containing ammonia does not hinder the detection of ammonia by the reaction when carried out as described above.

b) As the Cobaltinitrite. The determination of ammonia by reacting it with sodium cobaltinitrite $Na_3[Co(NO_2)_6]$ is carried out as with chloroplatinic acid. By this reaction 0.34 μg of ammonia can be detected at a limiting concentration of 1:3000. The presence of other ions in solution does not interfere.

Reactions for Potassium. On studying the character of the absorption by compounds of different cations with Karno's reagent $Na_3[Bi(S_2O_3)_3]$, we found that only potassium compounds absorb the ultraviolet at $\lambda = 365$ mμ. The other compounds absorb at 313 mμ and less. This enables potassium to be determined in the presence of other elements by means of Karno's reagent on a long wave screen, excited by light of $\lambda = 365$-380 mμ.

The Reaction was Carried Out as Follows. A drop of the test solution containing potassium was evaporated on a quartz microscope slide to dryness and a drop of the Karno reagent added to the residue. The appearance of needles colored red under the microscope, indicates the presence of potassium in the solution. This reaction which is also used for microcrystalloscopic analysis in visible light is made considerably more sensitive in the ultraviolet: the limit of identification becomes 0.7 μg instead of 2 μg and the limiting concentration can be decreased to 1:1500.

In spite of the fact that ammonium salts themselves do not give a precipitate with Karno's reagent and also do not absorb near the visible region, they appreciably decrease the sensitivity of this reaction.

Reactions for Sodium. The detection of sodium is carried out by a fluorescence method. As the result of the reaction between zinc uranyl acetate and sodium salts the yellow fluorescence becomes fixed in the precipitate of the octahedra of sodium zinc uranyl-acetate. The reagent solution itself does not fluoresce since chlorine ions and other ions have a quenching effect.

In order to carry out the reaction in the ultraviolet microscope fluorescent screens are used in conjunction with a UFS-2 light filter which transmits light of wave length $\lambda = 313$ mμ.

Procedure. A drop of test solution is placed on a quartz microscope slide side by side with a drop of zinc uranyl-acetate solution. After the two drops mix, the octahedra of sodium zinc uranyl-acetate separate out with a bright yellow-green color. This reaction is very sensitive. The limit of identification is 0.03 μg of Na and the limiting concentration 1:330000. Potassium and ammonium salts do not interfere.

Reactions for Iron. The reactions listed below are characteristic for ultraviolet microchemistry, since the detection of the element is carried out both in amorphous precipitates and in solutions by the formation of compounds which absorb the ultraviolet.

a) Detection of Iron in the Presence of Bivalent Tin. In the long wave length region of the ultraviolet only three hydrates exhibit selective absorption [i.e. of those studied by us (which included compounds of all the cations which are included in the general scheme of systematic qualitative analysis, with the exception of the rare elements)]. These are ferrous hydroxide, ferric hydroxide and stannous hydroxide. Ferrous hydroxide under these conditions is quickly oxidized by aerial oxygen. Thus there are two cations which mutually interfere during any attempt to detect one of them in the presence of the other in any given mixture. This may be overcome by using the property of stannous hydroxide of forming stannites with excess alkali; this is completely transparent to the ultraviolet while the ferric hydroxide absorbs ultraviolet intensely, so that it can be easily detected by the bright red color of the precipitate.

Procedure. A drop of the test solution is placed on a quartz microscope slide and 2-3 drops of 20% NaOH added. As a result only the ferric hydroxide remains as a precipitate, while the stannous hydroxide goes into solution as stannite. The precipitate is colored red under the microscope.

The limit of identification is 0.04 μg of iron at a limiting concentration of 1:25000, which exceeds the best microcrystalloscopic reaction in the visible spectrum, viz. the formation of Prussian blue in which the limit of identification is 0.07 μg of Fe at a limiting concentration of 1:14000 under the same conditions.

The limiting ratio of iron to tin at which this reaction is still possible for 0.04 μg iron is 1:125000.

b) Detection of Trivalent Iron in the Form of $FeAsO_4$. Of the arsenates, only ferric arsenate exhibits selective absorption in the long wave length part of the ultra violet. This enables ferric iron to be detected in the presence of other cations, and also in the presence of bivalent iron without a preliminary separation.

Procedure. A drop of the test solution is placed on a quartz microscope slide and a drop of potassium arsenate solution (0.5 N) placed side by side with it. When the two drops are mixed an amorphous precipitate is formed which contains all the cations with the exception of those of potassium, sodium and ammonium. If trivalent iron is present the precipitate is colored red under the microscope while if ferric iron is absent the precipitate is grey.

The limit of identification is 0.02 μg of iron at a limiting concentration of 1:70000. If the drop of test solution is preliminarily dried the sensitivity of this reaction increases considerably; it is possible to detect 0.005 μg of iron at a limiting concentration of 1:300000. This reaction is possible for the following ratios of other cations.

Fe^{3+} : Ba^{2+} = 1:75 for 0.04 μg Fe		Fe^{3+} : Co^{2+} = 1:30 for 0.04 μg Fe	
Fe^{3+} : Sr^{2+} = 1:45 for 0.04 μg Fe		Fe^{3+} : Cu^{2+} = 1:32.5" 0.04 μg Fe	
Fe^{3+} : Ca^{2+} = 1:40 for 0.04 μg Fe		Fe^{3+} : Hg^{2+} = 1:37.5" 0.04 μg Fe	
Fe^{3+} : Mn^{2+} = 1.27.5" 0.04 μg Fe		Fe^{3+} : Cd^{2+} = 1:12.5" 0.04 μg Fe	

c) Detection of Iron by Means of Ammonium Acetate. Acetates with the exception of ferric and ferrous acetates and silver acetate do not absorb in the ultraviolet. Absorption by acetates is displaced into the Schumann region. Silver acetate shows maximum absorption in the wave length range of 313-254 mμ. Moreover this compound decomposes rapidly under the influence of the ultraviolet to form metallic silver, which does not absorb in the ultraviolet. Thus it is possible to detect iron in the presence of all the remaining cations.

Procedure. A drop of saturated ammonium acetate is added to a drop of test solution. If iron is present the solution and precipitate of the basic acetate salts are colored red under the microscope. When no iron is present solution and precipitate are transparent to the ultraviolet. The reaction is fairly sensitive and enables 0.04 μg of iron to be detected at a limiting concentration of 1:24000. The limiting ratios of iron to other cations for which the reaction can be carried out without a preliminary separation are as follows.

$Fe:Mg^{2+}$ = 1:120 for 0.47 μg Fe		$Fe:Mn^{2+}$ = 1:118 for 0.47 μg Fe	
$Fe:Ba^{2+}$ = 1:750 " 0.47 μg Fe		$Fe:Cr^{3+}$ = 1:93 " 0.47 μg Fe	
$Fe:Ni^{2+}$ = 1:125 " 0.47 μg Fe		$Fe:Al^{3+}$ = 1:50 " 0.47 μg Fe	
$Fe:Co^{2+}$ = 1:126 " 0.47 μg Fe		$Fe:Zn^{2+}$ = 1:13 " 0.47 μg Fe	

d) Detection of Iron as $FeCl_3$. From the absorption curve of $FeCl_3$ (Fig.2) it is clear that this compound is very suitable for the direct identification of iron. No other chloride exhibits such sharp absorption in the neighborhood of the visible spectrum. This characteristic absorption was used by us for the identification of iron in test solutions.

Procedure. A drop of test solution is mixed with a drop of HCl. When iron is present the drop is colored a bright red under the microscope. Nor a single cation interferes with this reaction and its sensitivity is exceptionally high. It is possible to detect 0.006 μg of iron at a limiting concentration of 1:500000. Bismuth depresses the sensitivity as can be seen from the limiting ratios of iron to the other cations;

$Fe:Hg^{2+}$ = 1:581 for 4.7 μg Fe		$Fe:Ni^{2+}$ = 1:62 for 4.7 μg Fe	
$Fe:Bi^{3+}$ = 1:1 " 4.7 μg Fe		$Fe:Cr^{3+}$ = 1:37 " 4.7 μg Fe	
$Fe:Co^{2+}$ = 1:95 " 4.7 μg Fe			

Reactions for Cadmium in the Presence of Zinc. The majority of microcrystalloscopic reactions for cadmium in the visible part of the spectrum are unsuccessful when zinc is present, since zinc salts are formed as well as the characteristic cadmium precipitates, and they interfere with the color and form of the crystals of the cadmium salt, as a result of which the latter cease to be characteristic.

This drawback can be removed by using ultraviolet light.

a) Detection of Cadmium as Cadmium Sulfide. In contrast to zinc sulfide, cadmium sulfide strongly absorbs in the near ultraviolet. This enables cadmium to be detected without removal of zinc.

Procedure. A drop of sodium sulfide solution is added to a drop of the test

solution and the two mixed with a glass rod. If cadmium is present the large red crystals of cadmium sulfide can be seen under the microscope. 0.02 μg of cadmium can be detected at a limiting concentration of 1:44000 in the presence of zinc. The limiting ratio of cadmium to zinc is:

$$Cd^{2+}:Zn^{2+} = 1:20 \text{ for } 1.67 \ \mu g \ Cd^{2+}$$

b) Detection of Cadmium as Phosphate. Zinc phosphate does not absorb in the ultraviolet so that cadmium can be detected in the presence of zinc.

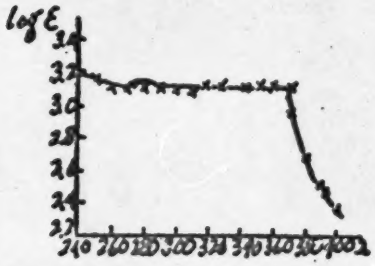

Fig. 2. Absorption curve for $FeCl_3$.

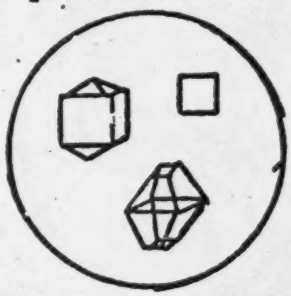

Fig. 3. Crystals of Cd-nitroprusside

Procedure. A drop of Na_2HPO_4 solution is added to a drop of test solution and the precipitate formed examined under the microscope. If cadmium is present the precipitate is colored red.

By this method it is possible to detect 0.18 μg Cd^{2+} at a limiting concentration of 1:6000 and a ratio of $Cd^{2+}:Zn^{2+}$ = 1:40 for 1.68 μg of cadmium.

c) Detection of Cadmium as the Nitroprusside. This reaction is the most sensitive of all the reactions for cadmium in the presence of zinc. It is based on the formation of characteristic crystals which absorb the ultraviolet at λ = 365-313 mμ (Fig.3).

Zinc in contrast to cadmium does not give a precipitate with sodium nitroprusside, and the solution does not absorb the ultraviolet at the given region of the spectrum.

Procedure. A drop of test solution is evaporated practically to dryness and a drop of a 1% solution of sodium nitroprusside added. The characteristic crystals which are formed are colored red when examined under the microscope.

The limit of identification is 0.01 μg of cadmium at a limiting concentration of 1:100000 and a limiting ratio of $Cd^{2+}:Zn^{2+}$ = 1:19 for 5.6 μg of Cd^{2+}.

In conclusion I wish to express my thanks to Doctor E. M. Broomberg and Yu. V. Morachevsky for valuable advice and daily help in carrying out the work.

SUMMARY

1. A microchemical method of analysis, based on the application of the ultraviolet microscope is described together with several examples.

2. The advantages of ultraviolet microscopy over ordinary microscopy are demonstrated by means of a number of examples.

3. Qualitative microchemical reactions are described for ammonium, potassium, iron and cadmium.

4. A qualititative luminescence reaction for sodium is described.

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USE OF THE LIQUID INTERFEROMETER IN QUANTITATIVE ANALYSIS

III. THE STUDY OF DILUTE SOLUTIONS OF HYDROLYZABLE SALTS

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In previous articles [1,2] we have described the use of the interferometer method for the determination of the concentrations of dilute aqueous solutions of strong and weak electrolytes using hydrochloric acid, caustic soda, oxalic, and acetic acids as examples. It was established in the course of this work that in the case of solutions of strong electrolytes within the concentration range employed, the so called phenomena of "breaks" can be observed and the curves relating the number of interference bands to the concentration for such solutions possess a stepwise character. Solutions of weak electrolytes do not exhibit the phenomena of "breaks", and the interference bands-concentration curves are straight lines, with some deviation from linearity for solutions of oxalic acid.

The aim of the present work is the study of the possibility of applying the interferometric method to the determination and control of the concentration of dilute aqueous solutions of hydrolyzable salts.

It could be assumed beforehand that interferometric measurements of these solutions would present certain difficulties which could only be solved experimentally. In addition, during investigations of sodium carbonate, and sodium bicarbonate solutions it was of interest to us to investigate the effect of hydrolysis on the linear relation between the number of interference bands and the concentration. The selection of these factors for investigation was determined by their significance in analytical practice and by the existing imperfect volumetric methods of determining the concentration of such solutions.

Study of Dilute Solutions of Sodium Carbonate. 25 solutions with concentrations ranging from 0.0025-0.16 N were prepared for interferometric measurements. Solutions of 0.001-0.1 N were prepared by dilution to standard volumes of an exactly 0.1 N solution of Na_2CO_3, and solutions greater than 0.1 N from a 0.2 N standard, prepared from chemically pure, dry Na_2CO_3 heated to a constant weight at 280-300°. The concentration of the Na_2CO_3 solutions were checked by potentiometric titration with HCl, the normality of which, 0.04812, was determined gravimetrically using $AgNO_3$ for precipitating the Cl ions.

Na_2CO_3 was titrated at 94-97° using a hydrogen electrode. The hydrogen was purified by passing it through washers of Ag_2SO_4, alkaline and acid $KMnO_4$ solutions.

It should be noted that although the potentiometric method of determining the equivalence point of Na_2CO_3 is more accurate and objective than the ordinary volumetric methods, nevertheless potentiometric titration is not free from errors. The liquid used for comparison was twice-distilled water from which the solutions used were prepared.

1) Deceased.

The Na_2CO_3 solutions were measured in a cell 19.91 mm long at 15±0.3°. The solutions were illuminated with white light, and the readings expressed on a drum scale in numbers of interference bands in a monochromatic green Hg light.

The other details of the method employed will not be dealt with further since they were described in detail in previous articles [3,4].

TABLE 1

Results of Measurements on Na_2CO_3 Solutions Expressed in Terms of N, Δn and Δn/c. Green Hg light, $\lambda = 546.07$ mμ at 15°

c(normality)	N' (Observed)	z	N (true)	$\Delta n \cdot 10^5$	$\frac{\Delta n}{c}$
0.002492	2.30	0	2.30	31.5	0.01266
0.010040	9.24	0	9.24	126.7	0.01262
0.015037	13.78	0	13.78	189.0	0.01257
0.020190	19.46	1	18.46	266.9	0.01254
0.039860	37.64	1	36.64	502.5	0.01261
0.044930	43.24	2	41.24	565.5	0.01258
0.080297	75.57	2	73.57	1009.0	0.01256
0.085490	81.19	3	78.19	1072.3	0.01254
0.10000	94.45	3	91.45	1254.1	0.01254
0.14634	135.81	3	132.81	1821.0	0.01245
0.16170	149.79	3	146.79	2013.0	0.01245
			Average		0.01256

Results are given in the abbreviated Table 1, from which a curve relating the number of interference bands to concentration can be derived (Fig.1).

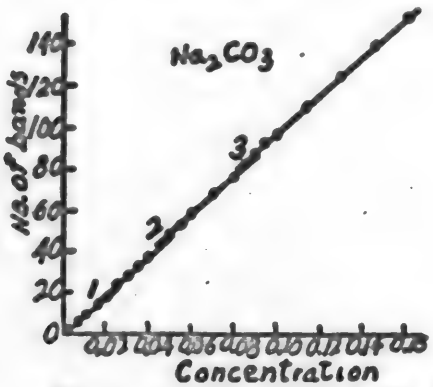

Fig. 1. Curve showing the relation between number of bands and concentration for Na_2CO_3 solutions.

In the table c is the concentration; N' – the observed number of bands; z – the number of bands corresponding to the number of breaks; N – the true number of bands with corrections for breaks; Δn – the difference between the refractive indices; and Δn/c the ratio of Δn to the concentration.

Analysis of the results from the table and graph show that for the Na_2CO_3 concentrations employed there are only three breaks; the first between the 15.77 and 19.46 bands (for an additional solution which was measured with c = 0.01759 N corresponding to the 15.7 band, no break was established); the second between the 37.64 and 43.24 band and the third after 75 bands.

During preliminary measurements the presence of a fourth break at a concentration of 0.1146 N corresponding to the 101.48 band was postulated. However the presence of this fourth band could not be demonstrated by confirmatory experiments.

A comparison of the results for Na_2CO_3 solutions with similar measurements on NaOH solutions (see the abbreviated Table 2, taken from previous articles [1]) shows that while in the case of NaOH for a similar concentration range the presence

of eight breaks was established, with a new cycle starting after 15 bands, this periodicity was not observed from Na_2CO_3 solutions, for which the first break only appeared after the 15.77 band, the second after the 37.64 band and the third after 75 bands.

It may be postulated that this anomaly in the number of bands and the absence of any periodicity in the case of Na_2CO_3 solutions is a direct result of hydrolysis.

TABLE 2

Results for Measurements on NaOH Solutions Expressed in Terms of N, Δn, $\Delta n/c$. Green Hg light $\lambda = 546.07$ mμ at 20°.

c(molarity)	N' (observed)	z	N (true)	$\Delta n \cdot 10^6$	$\frac{\Delta n}{c}$
0.001010	0.85	0	0.85	11.6	0.01150
0.010330	8.65	0	8.65	118.6	0.01148
0.020376	18.08	1	17.08	234.3	0.01149
0.039941	35.48	2	33.48	459.2	0.01149
0.060306	53.43	3	50.43	691.5	0.01147
0.071213	63.60	4	59.60	817.3	0.01147
0.10033	88.67	5	83.67	1147.4	0.01143
0.11974	105.72	6	99.72	1367.5	0.01142
0.13970	123.22	7	116.22	1597.5	0.01143
0.16027	141.52	8	133.52	1831.0	0.01142

The value of Δn is known to be additive and is dependent both on the number as well as on the nature of the particles in solution. The accumulation in Na_2CO_3 solutions of HCO_3^- and OH^- ions together with Na^+ and CO_3^{2-}, increase the light refracting capacity of its solutions as compared with NaOH solutions. It is characteristic that for very dilute Na_2CO_3 solutions in which the extent of hydrolysis is most significant, the period for the first break is roughly the same as for NaOH solutions of the same concentration.

An increase in the concentration of the Na_2CO_3 solutions which is followed by a decrease in the degree of hydrolysis leads to a significant increase in the value of N and Δn as compared with the corresponding values for similar concentrations of NaOH. This is also confirmed by comparing the values of $\Delta n/c$ which on an average is equal to 0.01256 for Na_2CO_3 solutions and 0.01146 for NaOH solutions.

This anomalous behavior of dilute solutions of Na_2CO_3 in relation to hydrolytic effects was also established by Geffcken [5] who studied the concentration relationship between the apparent molecular volumes and apparent molecular refractions in dilute solutions.

In spite of this anomalous behavior of dilute solutions of Na_2CO_3 the experimentally determined curve relating the number of interference bands to concentration, as shown by confirmatory experiments, can be used successfully for the interferometric determination of unknown concentrations of Na_2CO_3 solutions.

The Study of Dilute Solutions of Sodium Bicarbonate. Interferometric measurements were made on 21 solutions of $NaHCO_3$ in the concentration interval 0.005-0.150 N. The solutions of the concentrations indicated were prepared by dissolving the corresponding amount of solid $NaHCO_3$ in twice distilled, carbon dioxide-free water. The solid salt was preliminarily checked for purity and content of $NaHCO_3$.

A final check on the concentration of the solutions prepared was carried out gravimetrically, taking into account necessary corrections for weighing in air and the specific gravity of water, the concentration being expressed in molarities (number of moles in 1 kilogram of solvent).

As in the previous instance measurements of $NaHCO_3$ were carried out in a cell 19.91 mm long at 20±0.1° with subsequent conversion of the results of measurements made in white light into numbers of interference bands in green Hg light.

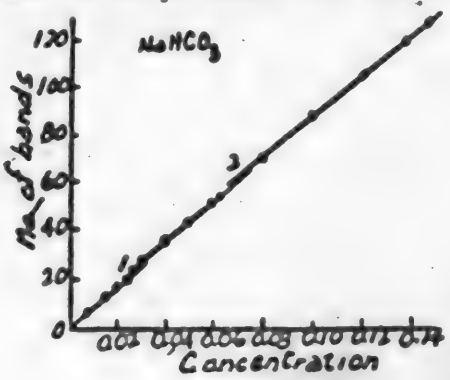

Fig. 2. Curve relating number of bands to concentration for $NaHCO_3$ solutions.

Results of these measurements are given in Table 3 in an abbreviated form, from which an interferometric curve relating the number of interference bands to concentration can be constructed.

Analysis of the tabulated results show that for $NaHCO_3$ solutions within the range of concentrations employed only two breaks could be established; the first at a concentration greater than 0.025 mol/l between the 21.22 and 26.7 bands and the second at a concentration greater than 0.068 mol/l, i.e. between the 59.71 and 62.06 bands.

The anomaly in the number of breaks and the absence of periodicity in the breaks which was found for $NaHCO_3$ as well as for the Na_2CO_3 solutions examined previously, is probably the result of hydrolysis.

TABLE 3

Results of Measurements of $NaHCO_3$ Solutions Expressed in Terms of N, Δn and $\Delta n/c$ Green Hg light, $\lambda = 546.07$ mμ at 15° C.

c (molarity)	N' (observed)	z	N (true)	$\Delta n \cdot 10^3$	$\frac{\Delta n}{c}$
0.004596	3.98	0	3.98	54.6	0.01187
0.010182	8.80	0	8.80	120.6	0.01185
0.024655	21.22	0	21.22	291.0	0.01180
0.029862	26.70	1	25.70	352.4	0.01180
0.068565	59.71	1	58.71	805.1	0.01174
0.070132	62.05	2	60.05	825.5	0.01174
0.12079	105.37	2	103.37	1417.5	0.01174
0.14758	128.85	2	126.25	1731.2	0.01173
			Average		0.01178

In spite of this anomaly, the difference in light refraction expressed as interference bands N and Δn with increasing concentration increase for $NaHCO_3$ solution in approximately the same sequence as for similar concentrations of NaOH solutions.

A comparison of the values of N and Δn for approximately equal concentrations of $NaHCO_3$ and Na_2CO_3 shows a significant increase in their values for Na_2CO_3 solutions. It is characteristic that the average value of $\Delta n/c$ for Na_2CO_3 solutions is considerably higher than that for $NaHCO_3$ solutions.

In our opinion the results adduced above agree, and confirm the difference

in the hydrolytic effect for equal concentrations of Na_2CO_3 and $NaHCO_3$. Just as the hydrolytic effect should not interfere with the possibility of using the interferometric method for the determination of Na_2CO_3 concentrations, it should not interfere with the interferometric determinations of $NaHCO_3$ concentrations.

SUMMARY

1. Interferometric measurements have been made on dilute aqueous Na_2CO_3 and $NaHCO_3$ solutions.

2. From the results the values of Δn and $\Delta n/c$ for the same solutions for Hg light of $\lambda = 546.07$ mμ have been calculated.

3. Significant deviations in the appearances of breaks in the interferometric curves of $\underline{N}$ against $\underline{c}$ was observed for Na_2CO_3 and $NaHCO_3$ solutions as compared with NaOH solutions.

4. It has been shown that the difference in these curves and the greater increase in the values of N, Δn and $\Delta n/c$ for Na_2CO_3 solutions and the smaller increase in the corresponding values for $NaHCO_3$, as compared with similar concentrations of NaOH are determined by the different extents of hydrolysis of these electrolytes..

5. Using Na_2CO_3 and $NaHCO_3$ as examples it has been confirmed experimentally that the interferometric method can be used for the determination and control of the concentrations of hydrolyzable salts.

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THERMODYNAMIC CRITERIA OF THE APPLICABILITY OF CHEMICAL REACTIONS OF VOLUMETRIC ANALYSIS

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There is no clear formulation in contemporary literature of the requirements which must be satisfied by chemical reactions used in volumetric analysis from the thermodynamic point of view. Most authors confine themselves to general observations about "reactions which proceed quantitatively", without investing this concept with any concrete content. Meanwhile, it is possible as shown below, to formulate clearly criteria for the applicability of different reactions in volumetric analysis by adopting a thermodynamic approach. Moreover, thermodynamic consideration of reactions which are the bases of volumetric-analytical determinations, enables all the branches of volumetric analysis to be combined and considered from a single view point.

As a rule in volumetric analysis reversible reactions are used in which the equilibrium is strongly displaced towards the side where formation of the reaction products occur:

$$n_1A_1 + n_2A_2 \rightleftarrows n_1'B_1 + n_2'B_2. \qquad (I)$$

From our point of view it is essential to follow the changes in concentration of two substances (the titrant and the material to be titrated) denoted by A_1 and A_2. A third component can participate in this reaction (H and OH ions), nevertheless in actual conditions the concentration of the third component is low and does not change very much during titration. In the majority of cases the change in ionic strength during titration is insignificant and therefore concentrations can be used instead of activities.

Of particular interest to the analytical chemist is the ratio at the equivalence point; at this point the respective reaction products (B_1 and B_2) which are formed in stoichiometric ratios are subject to a partial conversion into the original reactants:

$$n_1'B_1 + n_2'B_2 \rightleftarrows n_1A_1 + n_2A_2. \qquad (Ia)$$

The equilibrium constant of this reaction is a very important thermodynamic quantity which is related to the standard change in the thermodynamic potential (ΔZ°) by the relation:

$$\Delta Z^\circ = - RT \ln K. \qquad (1)$$

At 25° this equation becomes:

$$\Delta Z^\circ = - 1364 \log K \qquad (1a)$$

Let us consider the change in thermodynamic potential for reaction (Ia) in a system where the ratio of all the reactants is equal to the ratio of the stoichiometric coefficients of equation (Ia), i.e.

$$C_{A_1} = n_1a \quad C_{A_2} = n_2a \quad C_{B_1} = n_1'a \quad C_{B_2} = n_2'a. \qquad (2)$$

If we substitute these values of the concentrations in the equation for the

chemical reaction isotherm, we get[1]:

$$\Delta Z = RT\left(\ln\frac{(n_1a)^{n_1}(n_2a)^{n_2}}{(n_1'a)^{n_1'}(n_2'a)^{n_2'}} - \ln K\right). \qquad (3)$$

Equation (3) can be transformed by substituting logarithms to the base ten instead of the natural logarithms, multiplying out the logarithm and substituting numerical values for R and T (298° K):

$$\Delta Z = 1364[n_1 \log n_1 + n_2 \log n_2 - n_1' \log n_1' - n_2' \log n_2' + (n_1 + n_2 - n_1' - n_2') \log a - \log K]. \qquad (4)$$

The following abbreviations are then used:

$$\sum n \log n = n_1 \log n_1 + n_2 \log n_2 - n_1' \log n_1' - n_2' \log n_2', \qquad (5)$$

$$\sum n = n_1 + n_2 - n_1' - n_2', \qquad (6)$$

$$pK = -\log K. \qquad (7)$$

So that equation (4) may be rewritten in the condensed form:

$$\Delta Z = 1364\left(\sum n \log n + \log a \sum n + pK\right) \qquad (8)$$

or

$$\Delta Z = 1364\left(\sum n \log n + \log a \sum n\right) + \Delta Z^{\circ}. \qquad (9)$$

At the equivalence point the ratio of the concentration of reaction products B_1 and B_2 is equal to the ratio of the corresponding stoichiometric coefficients (n_1' and n_2').

The concentrations of these substances differ only by very little from the values calculated on the assumption of the absence of any conversion into the original reactants. The original reactants, as a result of reaction (1a) are also formed in strictly stoichiometric ratios. We shall introduce the following designations for the concentrations of the substances at the equivalence point[2]:

$$\bar{C}_{A_1} = n_1x \quad \bar{C}_{A_2} = n_2x \quad \bar{C}_{B_1} = n_1'a \quad \bar{C}_{B_2} = n_2'a. \qquad (10)$$

After substituting these values in the equation for the equilibrium concentrations of reaction (Ia) we get:

$$\frac{(n_1x)^{n_1}(n_2x)^{n_2}}{(n_1'a)^{n_1'}(n_2'a)^{n_2'}} = K. \qquad (11)$$

On taking logarithms of this equation and using the abbreviations (5) and (6) we get:

$$\sum n \log n + (n_1 + n_2) \log x - (n_1' + n_2') \log a = -pK. \qquad (12)$$

This equation can be used primarily for calculating the concentrations of reactants (A_1 and A_2) at the equivalence point. In accordance with the accepted designations:

$$\log\bar{C}_{A_1} = \log n_1 + \log x; \qquad (13)$$

$$\log\bar{C}_{A_2} = \log n_2 + \log x. \qquad (13a)$$

If we substitute the value of $\log x$ from equation (12) in these equations and simplify, we get an universal equation for calculating the concentrations of the

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1) From here onwards we are dealing with reactions which occur in condensed systems.
2) The equilibrium concentrations of B_1 and B_2 differ only very slightly from the initial concentrations because of the quantitative course of reaction (I).

reactants at the equivalence point:

$$\log \bar{C}_{A_1} = \frac{(n_1' + n_2')\log a - pK - \sum n \log n + (n_1 + n_2)\log n_1}{n_1 + n_2} \qquad (14)$$

or

$$\log \bar{C}_{A_1} = \frac{n_1' \log C^0_{B_1} + n_2' \log C^0_{B_2} + n_2 \log \frac{n_1}{n_2} - pK}{n_1 + n_2} \qquad (14a)$$

These equations can be used for calculating the concentrations of the reactants at the equivalence point for any volumetric method of analysis. The possibility of using any given reaction in volumetric analysis is determined by the magnitude of the reconversion of the reaction products (B_1 and B_2) into the reactants (A_1 and A_2). The extent to which this reconversion occurs is given by the relation:

$$\alpha = \frac{x}{a} . \qquad (15)$$

The value of this ratio defines the theoretical limit of the practicable accuracy for a given reaction. E.g., an accuracy of determination of $\pm 0.1\%$ can be achieved under conditions such that the extent of reconversion of the reaction products into the reactants (α) does not exceed 0.001. If decomposition of the reaction products to give reactants exceeds this value, then the accuracy of $\pm$ 0.1% cannot be achieved at the given temperature. Log α can be calculated from Equation (12). It is equal to:

$$\log \frac{x}{a} = \frac{-pK - \log a \sum n - \sum n \log n}{n_1 + n_2} \qquad (16)$$

By means of this equation the limiting practicable accuracy for any volumetric method of analysis can be calculated.

Since the accuracy of volumetric determinations amounts to $\pm 0.1\%$, then the conditions for realizing this accuracy can be formulated as follows:

$$\log \frac{x}{a} < -3 \qquad (17)$$

The value of log x/a can be taken from Equation (16), from which:

$$pK + \log a \sum n + \sum n \log n > 3(n_1 + n_2). \qquad (18)$$

By comparing this equation with Equation (8), we get:

$$\Delta Z > 3 \cdot 1364 \cdot (n_1 + n_2). \qquad (19)$$

The inequalities of (17), (18), and (19) express the possibility of carrying out a titration based on the use of a given reaction with an accuracy of $\pm$ 0.1%. A more simple formulation of this possibility can be derived from Equation (19).

The change in thermodynamic potential in process (1a), in a system where all the reactants are at concentrations corresponding to those at the equivalence point, should exceed a definite value. E.g., in a simple case during the formation of a substance AB, the value of ΔZ should exceed 8184 calories.

The possibility of using a given reaction in volumetric analysis is determined by the values of the equilibrium constant of reaction (Ia) (it should have a minimum value), and by the concentration of the reactant at the equivalence point (maximum values).

All the equations given above and all the arguments advanced are true for titration reactions and do not apply to reactions preceding titration (preliminary precipitations, separation, changes in the degree of oxidation, etc.).

Let us consider one of the most important and most often used special cases - a reaction of the type[1]:

$$A + nB = ABn, \qquad (II)$$

in this case $\sum n \log n = n \log n$ and $\sum n = n$.

Equations (14) and (18) are simplified considerably in this special case. If we substitute and take into account (2), we get

$$\log \bar{C}_A = \frac{\log C_A^0 - pK - n \log n}{n + 1}; \qquad (14a)$$

$$\log \bar{C}_B = \frac{\log C_B^0 - pK}{n + 1}; \qquad (14b)$$

$$pK + n \log C_B^0 \geqslant 3(n + 1) \qquad (18a)$$

In these equations $\bar{C}_A$ and $\bar{C}_B$ represent the equilibrium concentrations, and C_A^0 and C_B^0 the hypothetical concentrations of A and B at the equivalence point under such conditions that there is no interaction between them. C_A^0 and C_B^0 are the initial concentrations of A and B.

We shall demonstrate the applicability of these equations for determining the possibility of using different reactions in volumetric analysis and for calculating the ratios at the equivalence point for a number of cases. For the titration of a strong acid with a strong base or vice versa the reaction proceeds according to the equation:

$$H^+ + OH^- = H_2O. \qquad (III)$$

The concentration of water formed during this reaction remains practically unchanged during titration, and the concentration of water is therefore not included in the equation for the equilibrium constants, in this case:

$$n_1 = n_2 = 1, \quad \sum n = 2, \quad \sum n \log n = 0.$$

Here, $pK = 14$.

Substituting these values in Equations (14) and (18) we get:

$$\log \bar{C}_H = -7, \qquad \log C_H^0 \geqslant -4. \qquad (18b)$$

In reaction (III), therefore, the concentrations of the reactants should be more than 0.0001 M.

The titration of weak acids with strong bases proceeds in the majority of cases according to the equation:

$$HA^z + OH^- = A^{z-1} + H_2O, \qquad (IV)$$

The equilibrium constant for reactions involving the conversion of A^{z-1} into the reactants is equal in this case, as is well known, to the hydrolysis constant:

$$K_h = \frac{K_W}{K_A}, \qquad (20)$$

where K_W is the ionic product of water, and K_A is the ionization constant of acid HA^z. From which it follows for process (IV):

$$pK_h = 14 - pK_A. \qquad (21)$$

The concentration of H_2O is not included in the equation of the law of mass

[1] From this point onwards we shall consider the equilibrium constants of the reverse reaction, i.e., the decomposition of AB_n into its components in this actual given instance.

action for Reaction (IV), and according to Equation (14a) for the equivalence point we get the well-known relation:

$$\log \bar{C}_{OH} = \frac{\log C^0_{OH} + pK_A - 14}{2} . \qquad (14c)$$

From Equation (18a) the following conditions for the accurate titration of weak acids can be derived:

$$pK_A - \log C^0_{OH} \leqslant 8. \qquad (18c)$$

If decinormal solutions are used and the volume is assumed to remain unchanged during the titration,

$$pK_A \leqslant 7.$$

It is therefore only possible to titrate with accuracy those acids whose ionization constants are greater than 10^{-7} ($pK_A \leqslant 7$), e.g., the following acids: HF (3.14); H_2S (6.48); H_2CO_3 (6.43); H_3PO_4 (2.12); $H_2PO_4^-$ (7.21); HCOOH (3.75); CH_3COOH (4.76), etc. (The values of pK_A are given in brackets).

Exact titrations of the following acids cannot be realized in 0.1 N solutions: HCN (9.14); H_3BO_3 (9.24); C_6H_5OH (9.89); HCO_3^- (10.24); H_2O_2 (11.62); HIO_3 (10.7); HPO_4^{2-} (12.3); HS^- (14.70), etc. From Equation (16) it follows, e.g., that H_3BO_3 in 0.1 M solution can be titrated with an accuracy of $\pm$ 1.3%. For the titration of salts of weak acids with strong acids according to the equation

$$A^{z-1} + H^+ = HA^{z-1} \qquad (V)$$

the equilibrium constant is equal to the ionization constant of the acid HA^z. By using Equation (14a) for the hydrogen ion concentration at the equivalence point, we get the following relation:

$$\log \bar{C}_H = \frac{\log C^0_H - pK_A}{2} . \qquad (14d)$$

The possibility of titrating according to Equation (V) is determined by Equation (18a); in this case we get

$$pK_A + \log C^0_H \geqslant 6 . \qquad (18d)$$

If 0.1 N solutions of acid are used, then

$$pK_A \geqslant 7.$$

When using decinormal solutions it is possible to attain the necessary accuracy ($\pm$ 0.1%) only for salts of acids for which the ionization constant is less than 10^{-7}.

Examples are given below of anions, the concentration of which can be determined in 0.1 N solution (the values for pK_A are given in brackets): CN^- (9.14); CO_3^{2-} (10.24); HCO_3^- (6.43); HS^- (6.48)[1]; C_6H_5OH (9.89), etc. It is impossible to realize by means of Equation (V) an exact determination in 0.1 N solutions of the ions: F^-, CH_3COO^-, $C_6H_5COO^-$, etc. From Equation (16) it follows, e.g., that an acetate in 0.1 M solution can be titrated with an accuracy of $\pm$ 1.3%. For weak bases reacting with strong acids according to the scheme:

$$B + H^+ = BH^+, \qquad (VI)$$

the equilibrium constant of the reaction is determined by the conversion of BH^+ into the original components, and is equal to:

$$K = \frac{K_W}{K_B} \qquad (20a)$$

1) For HCO_3^- and HS^- the accuracy of the titration is approximately 0.2%.

from which

$$pK = 14 - pK_B \ . \qquad (21a)$$

The hydrogen ion concentration at the equivalence point can be calculated by means of Equation (14a):

$$\log \bar{C}_H = \frac{\log C_H^0 + pK_B - 14}{2} \ . \qquad (14e)$$

Substituting the value of pK in Equation (18c), then in this case we get:

$$pK_B - \log C_H^0 \leqslant 8. \qquad (18e)$$

For decinormal solutions: $pK \leqslant 7$. According to (IV) it should be possible to titrate accurately by means of 0.1 N solutions only in those cases when the ionization constant of the base is fairly high and exceeds 10^{-7}. This requirement is satisfied by NH_3 (4.75), $C_2H_5NH_2$ (3.25), $HOCH_2CH_2NH_2$ (4.56), etc. It is not possible to titrate the following bases accurately in 0.1 N solution by means of a strong acid: pyridine (8.85); aniline (9.42); acetamide (12.60); urea (13.82); thiourea (14.96); etc. (the figures in brackets are the pK_B values).

Complex-formation reactions, which are being used more widely of late in volumetric analysis, proceed according to the scheme:

$$M^{z+} + nA^{x-} = [MA_n]^{z-nx} \ . \qquad (VII)$$

The equilibrium constant of the decomposition reaction of the complex ion to form its components is the instability constant (K_n), and accordingly $pK = pK_H$. The concentrations of the metal ion (M^{z+}) and the addendum A^x at the equivalence point can be calculated from Equation (14a). In this case we have:

$$\log \bar{C}_{M^{z+}} = \frac{\log C_M^0 - pK_H - n \log n}{n+1} \ ; \qquad (14f)$$

$$\log \bar{C}_{Ax-} = \frac{\log C_A^0 - pK_H}{n+1} \ . \qquad (14g)$$

The possibility of using complex-formation reactions for volumetric analysis calculation is determined by the following inequality which is derived by substitution of the value of pK_H in the inequality (18a)

$$pK_H \geqslant 3n + 3 - n \log C_B^0 \ . \qquad (18f)$$

If the concentration of the original solution of the addendum (A^{x-}) is 0.1 M, then

$$pK_H \geqslant 4n + 3,$$

i.e., for complexes with different coordination numbers pK_H should be greater than some definite value. In the case of a salt of the type MA^{z-x}, $pK_H \geqslant 7$; for a coordination number of 2, $pK_H \geqslant 11$; for a complex of the type MA_3^{z-3x}, $pK_H \geqslant 15$, and, finally, in the case of a complex of the type MA_4^{z-4x}, $pK_H \geqslant 19$.

Titrations based on the formation of the following complexes can be carried out in solutions 0.1 M with respect to the addendum (the values of pK_H are given in brackets): $FeHPO_4^+$ (9.35); $HgCl_2$ (12.8); $HgBr_2$ (17.3); $Ag(CN)_2^-$ (21); $Cu(NH_2CH_2COO)_2$ (15.3); $Zn(OH)_3^-$ (14.4); $Cd(CN)_4^{2-}$ (18.8); $TlCl_4^-$ (18.4);, etc.

Accurate titrations on the basis of the formation of the following complexes, however, cannot be carried out in 0.1 M solution with respect to the addendum: CdI_4^{2-} (6.0); $Cd(S_2O_3)_3^{4-}$ (7.0); $FeCNS^{2+}$ (2.40); $Cu(NH_3)_4^{2+}$ (12.7), etc.

The relations given above are also applicable for calculation when precipitation reactions are used in volumetric analysis. Almost all precipitation

reactions which are in use proceed as follows:

$$M^{z+} + nA^{x-} = MA_n\downarrow \quad . \qquad \text{(VIII)}$$

The concentrations of the metal cations and anions A^{x-} at the equivalence point can be calculated by substituting the respective values in Equation (14).

The decomposition of the precipitate formed to give the original reactants is characterized by the solubility product of the salt, $MA_n(Lp)$. The reciprocal of the logarithm of the solubility product is denoted by pLp. After substitution of this value in Equation (14) and simplifying, we get:

$$\log \bar{C}_M = \frac{-pLp - n \log n}{n+1} \quad ; \qquad \text{(14h)}$$

$$\log \bar{C}_A = \frac{-pLp + \log n}{n+1} \quad . \qquad \text{(14i)}$$

The possibility of using a given precipitation reaction for volumetric analysis is determined by the Inequality (18). For reaction (VIII):

$\sum n \log n = n \log n$, a $\sum n = n + 1$. Having worked out (2), substituting in Equation (18) all the values, and simplifying, we get:

$$pLp + n \log C_A^0 + \log C_M^0 \geqslant 3(n+1). \qquad \text{(18g)}$$

If solutions are used with $C_M^0 = 0.1$ and $C_X^0 = 0.1\,n$, we get

$$pLp + n \log n \geqslant 4(n+1).$$

For salts of type MA, pLp should be greater than 8, and in the case of salts of type MA_n, pLp should be greater than 11.4. It should be borne in mind that we are considering titrations to an accuracy of 0.1% of solutions 0.1 N or 0.1 M with respect to the metal. The formation of the following salts satisfies this requirement: AlCl (9.81); AgBr (12.11); AgI (15.82); $BaSO_4$ (9.97); $PbCrO_4$ (13.74); Hg_2Cl_2 (17.96); Hg_2Br_2 (22.3); $Hg_2(CNS)_2$ (19.52); $Pb(IO_3)_2$ (12.52), etc. The formation of the following salts does not satisfy this requirement: $SrSO_4$ (6.55); TlCl (3.72); $PbBr_2$ (5.20); PbI_2 (8.06), etc.

Equations (16), (18), and (19) can also be used for calculations involving oxidation-reduction reactions. Let us consider one of the most commonly used cases:

$$n_1 \text{ oxid.}_1 + n_2 \text{ reduc.}_2 = n_1 \text{ reduc.}_1 + n_2 \text{ oxid.}_2. \qquad \text{(IX)}$$

In this case $\sum n \log n$ and $\sum n$ become zero. The logarithm of the equilibrium constant is related to the oxidation-reduction potential by the simple relation:

$$pK = \frac{(\pi_2 - \pi_1)v}{0.058} \quad . \qquad \text{(22)}$$

Equation (22) can be applied to reactions which proceed at a standard temperature; π_2 and π_1 are the oxidation-reduction potentials, and v is the number of donated (or accepted) electrons.

Using Equation (16), we find that at the equivalence point

$$\log C^0_{\text{oxid.}_1} = \frac{(\pi_2 - \pi_1)v}{0.058(n_1 + n_2)} + \log C^0_{\text{oxid.}} \qquad \text{(14j)}$$

In order to establish the possibility of using any given oxidation-reduction reaction in volumetric analysis, we use Equation (18). In this particular case it is transformed into the following equations:

$$\frac{(\pi_2 - \pi_1)v}{0.058} \geqslant 3(n_1 + n_2) \qquad \text{(18h)}$$

and

$$\pi_2 - \pi_1 > \frac{0.174(n_1 + n_2)}{v} \quad (181)$$

The possibility of using a given reaction in volumetric analysis is determined by the potential difference. A change in pH and other conditions is connected with a change in the oxidation-reduction potentials, and is taken into account in the value of the normal potentials, which are related to a strictly defined pH value.

In conclusion the author should like to observe that is is possible to consider all volumetric analysis methods from one point of view by means of the equations adduced. We think that the wide use of the Inequalities (18) and (19) will considerably facilitate the search for new analytical reactions and will enable the possible limits of the application of reactions already in use in volumetric analysis to be defined more clearly.

SUMMARY

1. A universal equation for calculating the concentrations of the reactants at the equivalence point is proposed. This equation is applicable for calculating concentrations in reactions involving neutralization, complex formation, precipitation, and oxidation-reduction, respectively.

2. Universal inequalities are proposed which determine the possibility of using any given reaction in volumetric analysis, in which a determination can be carried out with a given degree of accuracy (examples are given of reactions in which accuracies of $\pm$ 0.1% are required). These inequalities are applied to concrete cases in methods based on neutralization, complex formation, precipitation, and oxidation-reduction reactions, respectively.

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A COLORIMETRIC METHOD FOR THE DETERMINATION OF IRON

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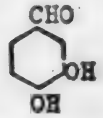
Aqueous solutions of protocatechuic acid (3,4-dihydroxybenzoic acid-1) — $C_6H_3(COOH^1)(OH^3)(OH^4)$ — [1], and of protocatechuic aldehyde  [2] are known to give a very characteristic reaction with ferric chloride: a green color appears initially, which on addition of a weak alkali solution first turns into a violet color and finally into a red color.

Lutz [3] used protocatechuic acid for detecting iron. The author shows that by means of an aqueous solution of protocatechuic acid it is possible to detect 0.24 μg of Fe^{3+} in 1 ml of solution in a weakly acid medium at a limiting dilution of 1:4,200,000, while in a weakly alkaline medium 0.1 μg Fe^{3+} in 1 ml can be detected at a limiting dilution of 1:10,000,000. Protocatechuic acid reacts in a similar manner with salts of Tl and Ce.

In the present work the reactive capacity of protocatechuic aldehyde with salts of trivalent iron has been examined, and the sensitivity and specificity of the given reaction determined. It was established that the color obtained at low concentrations 25 - 0.5 μg of trivalent iron in 1 ml of solution with protocatechuic aldehyde in alkaline media follows the Lambert-Beer law. This fact was used as the basis of a new colorimetric method for the determination of iron in metallic aluminum and zinc and in salts of the alkali and alkaline-earth metals respectively.

EXPERIMENTAL

Detection of trivalent iron in weakly acid media. To 1 ml of the test solution are added 0.1 ml of 1% HCl, 0.1 ml of a 0.25 aqueous solution of protocatechuic aldehyde, and the mixture shaken. After 5-10 minutes a color is observed. If trivalent iron is present, the color developed is an intense green color for large concentrations, and a pale violet color for low concentrations.

0.5 μg of Fe^{3+} in 1 ml solution can be detected in this way in a weak acid medium at a limiting concentration of 1:2,000,000.

Detection of trivalent iron in weakly alkaline media. To 1 ml of the test solution are added 0.1 ml of 1% ammonia, 0.1 ml of a 0.25% aqueous solution of protocatechuic aldehyde, and the mixture shaken. A blank test is made simultaneously, i.e., the same volumes of the above reagents are added to 1 ml of distilled water, the mixture shaken and after 5-10 minutes the color of the test solution and blank solution are compared. If Fe^{3+} is present in large amounts the color developed is an intense red, while at low concentrations the color is orange yellow. The blank is simply colored yellow. When the reaction is carried out in weak alkaline media it is impreative that a blank be done because the reagent itself gives a yellow color with alkali.

In weak alkaline medium 0.2 μg of Fe^{3+} in 1 ml solution can be detected at a limiting concentration of 1:5,000,000.

The following cations and anions do not react with protocatechuic aldehyde and therefore do not interfere with the detection of trivalent iron-alkali and alkaline earth metals: Mg, Be, Al, Zn, Cd, Cu^{2+}, Hg^{2+}, Mn^{2+}, Co, Ni, Th^{4+}, Zr^{4+}, La^{3+}, I^{+}, Er^{3+}, Nb, Ta, Au, Pd, Pt, Ti^{2+}, Sn^{2+}, Ag, AsO_4^{3+}, PO_4^{3+}, WO_4^{2-}, Fe^{2+}.

Bivalent iron does not react with either protocatechuic acid or aldehyde. Lutz [3] is in error when he indicates that protocatechuic acid reacts with bivalent iron.

Elements which form precipitates with alkali do not interfere with the detection of iron, since if iron is present a red or orange yellow color develops in the transparent layer above the precipitate, while in the blank a yellow color appears. Naturally it is best to use approximately the same amounts of the elements which form precipitates with alkali in the blank. The elements enumerated above do not interfere with the detection of iron at ratios to Fe^{3+} of 3,000 : 1.

Only MoO_4^{2-}, VO_3^{-}, and Ce^{3+} react with protocatechuic aldehyde. Molybdenum reacts with aqueous solutions of protocatechuic aldehyde only in neutral media, giving an orange color at large concentrations and a pale yellow one at low concentrations. The sensitivity of this reaction is 0.2 μg of molybdenum in 1 ml at a limiting concentration of 1:5,000,000. Molybdenum does not react in weakly acid solution.

Vanadium salts react in neutral media to give a dark brown color, and at low concentrations a violet brown color.

In weak HCl solution vanadium initially gives a rose color which is transformed after 10-15 minutes into a yellow color.

The sensitivity of the reaction for vanadium both in neutral and in acid media is 1 μg of vanadium in 1 ml solution at a limiting concentration of 1:1,000,000.

Salts of trivalent cerium only react with protocatechuic aldehyde in a weak ammonia solution, giving a red-brown color at high concentration and a yellow-brown color at low concentrations.

The sensitivity of the reaction is 4 μg of Ce^{3+} in 1 ml solution at a limiting concentration of 1:250,000.

Ce^{3+} does not react in acid media.

Colorimetric determination of trivalent iron. Standard solutions of trivalent iron are prepared containing 0.02 g Fe in 1 ml. 0.25 μg of chemically pure metallic iron is dissolved in 5 ml nitric acid diluted with 10 ml of water. The solution thus obtained is diluted to 1 liter (Solution A), 40 ml Solution A are diluted to 500 with water (Solution B). Solution B contains 0.02 mg of Fe in 1 ml.

Colorimetric determination of iron in metallic aluminum.

0.1 - 0.2 g of metallic aluminum (according to the iron content) is weighed out into a 50 ml beaker and 10 ml HCl (1:3) added. The beaker is covered with a watch glass, and slightly heated by alternately placing it on a hot plate and removing it until all the aluminum is dissolved when the solution is cooled to 40-50° and 1 ml of 3% H_2O_2 added to oxidize the Fe^{2+}. The beaker and its contents are then placed on a hot plate and the contents boiled for 5-10 minutes to decompose excess H_2O_2. The contents are transferred quantitatively to a 100 ml standard flask, made up to the mark with water and carefully mixed. 5 or 20 ml aliquots (according to the amount of iron) are transferred to a 50 ml standard to which 2 ml of a 0.25% solution of protocatechuic aldehyde is added.

The solution in the flask becomes colored green immediately. A solution of 10% NaOH is then added dropwise with continuous shaking until all the aluminum hydroxide precipitate has dissolved. When this has been accomplished the color of the solution and precipitate changes from a green through violet to a raspberry or orange-yellow color.

When all the precipitate has dissolved, water is added to the colored, transparent solution to bring the volume up to the mark, after which it is carefully shaken. The solution is then ready for color comparison.

At the same time 5 or 10 ml of the standard iron solution – solution B – are introduced respectively into a 50 ml standard flask, 2 ml reagent, and 0.5 ml of 10% NaOH are added and the whole made up to volume with water and throughly mixed. The color of the test solution and blank are compared in a Duboscq colorimeter.

By means of this method the iron content of 12 samples of aluminum was determined (Table 1). For comparison the iron content was determined in the same samples by a colorimetric method based on sulfosalicylic acid in ammoniacal solution by means of which both Fe^{2+} and Fe^{3+} were determined colorimetrically [4, 5, 6, 7].

It is necessary to point out that it is best to determine iron colorimetrically by means of protocatechuic aldehyde in alkaline solution. In acid media the color intensity (green light) is small for low concentrations, so that colorimetric determination is difficult.

TABLE 1

Iron content in percent		
Results of factory laboratory analysis	Colorimetric determination	
	With protocatechuic aldehyde	With sulfosalicylic acid [1]
0.79	0.80	0.76
0.35	0.34	0.32
0.28	0.28	0.27
0.14	0.13	0.13
1.57	1.58	1.60
0.29	0.32	0.30
0.18	0.20	0.21
0.13	0.15	0.15
0.14	0.15	0.13
0.82	0.85	0.80
0.70	0.69	0.68
0.93	1.06	1.09

The results in Table 1 show that the colorimetric determination of iron with protocatechuic aldehyde in alkaline solution gives results in good agreement both with the results of the sulfosalicylic acid method and with the results of factory analyses. The method proposed can be succesfully applied to the determination of iron in metallic aluminum. One determination takes 40-50 minutes.

The colorimetric determination of iron in metallic zinc.

1 g of metallic zinc or powder is put into a 50 ml beaker, 15 ml of dilute HCl are added (1:2) and the beaker covered with a watch glass. The beaker is gently heated by alternately placing it on and removing it from a hot plate, until the zinc has dissolved completely, when it is cooled to 40-50° and 1 ml of H_2O_2 added to oxidize the Fe^{2+}. The beaker's contents are boiled for 5-10 minutes to remove excess H_2O_2 and the contents finally quantitatively transferred to a 50 ml standard flask. 2 ml of a 0.25% solution of protocatechuic aldehyde is added and 10% NaOH solution added dropwise until all the zinc hydroxide dissolves. The colored, transparent solution thus obtained is made up to the mark with distilled water and carefully shaken, after which it is ready for colorimetric comparison.

At the same time 5 ml of the standard iron solution – Solution B – is introduced into a standard flask together with 4 ml reagent and 0.5 ml of a 10% solution of NaOH, made up to the mark with water and carefully shaken. The colors of the test and blank solution are compared in a Duboscq colorimeter. 0.004% iron can be determined in 1 g of zinc by this method. Duplicate determinations give good agreement

1) Part of the work with sulfosalicylic acid was carried out by A.I.Zaikin, to whom I express my thanks

In order to check the accuracy of the method experiments were carried out in which metallic zinc samples previously analyzed were taken and known amounts of iron in solution added after dissolution of the zinc. After oxidation, reagent and alkali were added, the volume made up to a standard and the total iron content determined by the method described above. The results of these tests are given in Table 2.

TABLE 2

Designation of test sample	Iron content in percent	Iron added in percent	Total iron in percent	Iron found
Granulated zinc, tech	0.015	0.008	0.023	0.022
Granulated zinc, Anal. Grade	0.006	0.002	0.008	0.008
Granulated zinc (Kahlbaum) free from arsenic	0.004	0.004	0.008	0.007
Zinc dust, tech.	0.008	0.004	0.012	0.011
Zinc dust, Anal. Grade.	0.006	0.002	0.008	0.008
Zinc dust (Kahlbaum) Anal. Grade	0.006	0.004	0.010	0.010

The colorimetric determination of iron in salts of the alkali and alkaline earth metals

2 g of the salt is weighed into a beaker, dissolved in 10-15 ml of water and 2-3 drops of conc. HNO_3 added to dissolve and oxidize the iron. The solution is quantitatively transferred to a standard 50 ml flask, 2 ml of a 0.25% aqueous solution of protocatechuic aldehyde and 5-6 drops of 10% NaOH are added, the volume made up to the mark with water and carefully mixed.

At the same time 5 ml of the standard iron solution – Solution B– is measured into a 100 ml flask and 4 ml reagent, and 2-3 drops of 10% NaOH added. The volume is made up to the mark with water and shaken thoroughly. The colors of test and blank solution are compared in a Duboscq colorimeter. 0.004% iron can be determined in 2 g of the salts of the alkali and alkaline earth metals. Duplicates are in good agreement.

In order to check on the accuracy of the method experiments were carried out in which salts were used containing a known amount of iron and to these were added a known weight of iron in solution. The total iron was then determined by the colorimetric method described above. The results are given in table 3.

TABLE 3

Designation of test sample	Iron content in percent	Iron added in percent	Total iron in percent	Iron found in percent
Sodium chloride, tech	0.008	0.004	0.012	0.011
Sodium chloride, Anal. grade	0.004	0.002	0.006	0.006
Magnesium chloride, tech.	0.010	0.008	0.018	0.017
Magnesium chloride, Anal. grade	0.004	0.004	0.008	0.008
Calcium chloride, tech.	0.012	0.008	0.020	0.020
Barium chloride, tech.	0.010	0.004	0.014	0.012

The method gives good results. The total iron found in most cases corresponds to the amount taken. The deviations observed in some cases are very small considering the very low iron content.

SUMMARY

1. A new color reaction is proposed for the determination of trivalent iron, which is based on the development of a color on interaction with protocatechuic aldehyde $(OH)_2 \cdot C_6H_3 \cdot CHO$.

The limit of identification in acid media is 0.5 μg Fe in 1 ml solution, and in alkaline media 0.2 μg in 1 ml solution. The majority of the elements at concentrations 3000 times that of the iron do not interfere MoO_4^{2-}, VO_3^-, and Ce^{3+} give the colors with the reagent.

2. It has been established that the color obtained by the interaction of low concentrations of trivalent iron for 25-0.5μg in 1 ml, with protocatechuic-aldehyde in alkaline media conforms to the Lambert-Beer law. On this basis therefore a new colorimetric method for the determination of iron has been worked out.

3. This colorimetric method has been worked out for the determination of iron in metallic aluminum, and zinc, and in the salts of the alkali and alkaline earth metals.

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THE USE OF DIANTIPYRYLPHENYLMETHANE IN ANALYTICAL CHEMISTRY. 2

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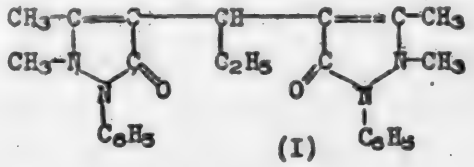
We have shown previously how diantipyrylphenylmethane (I) can be used for the volumetric and gravimetric determination of vanadium:[1]



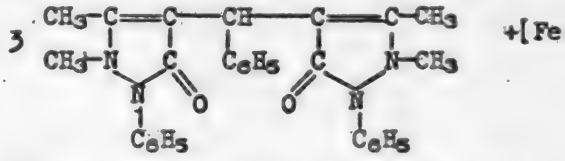
(I)

Further work has demonstrated that diantipyrylphenylmethane under certain conditions gives insoluble or almost insoluble precipitates with the anions $[Fe(CN)_6]^{3-}$, $[Fe(CN)_5\,NO]^{2-}$, $[Co(CN)_6]^{3-}$, and also $Cr_2O_7^{2-}$, $[Co(NO_2)_6]^{3-}$ and some others. In these cases the base (I) reacts with the respective complex acids forming salts of the "ammonia" type with high molecular weights.

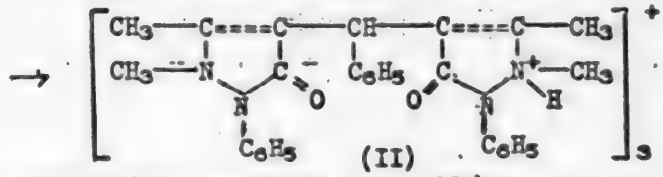
In the present article results are given for the quantitative determination of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ by means of diantipyrylphenylmethane, and the compounds formed are described.

Gravimetric Determination Of $[Fe(CN)_6]^{3-}$ With Diantipyrylphenylmethane

When an alcoholic solution of diantipyrylphenylmethane hydrochloride reacts with a solution of $K_3[Fe(CN)_6]$ in a weak acid medium, rapid formation of a greenish-yellow crystalline precipitate of the composition $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]\cdot 9H_2O$ occurs according to the following reaction



$+[Fe(CN_6)]^{3-} + 3H^+ \longrightarrow$



$[Fe(CN)_6]^{3-}$

(II)

(for the crystal form see Plate, page 291)

On heating to 100-120° the compound loses its water of crystalization but not its crystalline structure; the product thus obtained is of a brown color, which clinkers at 138-140° to a black mass.

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1) Gusev, Beiles and Sokolova, The Quantitative Determination of Vanadium by Means of Diantipyrylphenylmethane. J. Anal. Chem. 6, No. 1, p. 43 (1951).

This black mass decomposes with swelling at 155-160°. The compound (II) dissolves in alkalis and strong acids, with gradual separation of diantipyrylphenylmethane; the $[Fe(CN)_6]^{3-}$ ion can be detected in solution; (II) is soluble in 96° alcohol, but precipitates out on addition of water.

For analytical purposes it is essential that the $[Fe(CN)_6]^{4-}$ ion should not react with diantipyrylphenylmethane.

Analysis of the compound prepared (II)

Weight taken, in g	Weight of products obtained, in g	Found percent
0.1016	CO_2—0.2590	C—69.57
0.1120	CO_2—0.2849	C—69.42
0.1016	H_2O—0.0489	H— 5.39
0.1120	H_2O—0.0534	H— 5.31
0.7330	Fe_2O_3—0.0374	Fe— 3.57
0.6960	Fe_2O_3—0.0360	Fe— 3.62

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]$ Calculated C - 69.51%; H - 5.46%; Fe - 3.47%.

Determination of water of crystallization

1.0006 g after drying yielded 0.9082 g.

Found percent: H_2O - 9.23 For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]\cdot 9H_2O$. calculated percent: H_2O - 9.16.

In the quantitative determination of $[Fe(CN)_6]^{3-}$ it is necessary to carry out the analysis so that towards the end of precipitation the solution contains 50% alcohol, since under these conditions the precipitate of the complex is insoluble while the excess reagent (I) is kept in solution.

The high molecular weight of the compound enables small amounts of $K_3[Fe(CN)_6]$ to be determined.

a Gravimetric determination of $K_3[Fe(CN)_6]$. To 5 ml of a solution of $K_3[Fe(CN)_6]$ containing 0.025 g of the salt, are added 7 ml water, 3-4 drops of 2 N H_2SO_4 and 12 ml of a 2% alcoholic solution of diantipyrylphenylmethane. A precipitate is immediately formed which after 15 minutes is filtered under vacuum into a sintered glass funnel, the residue is washed from the beaker onto the funnel with filtrate and the precipitate finally washed with 25% aqueous alcohol (10-15 ml) and subsequently with water acidified with nitric acid (4 drops 1 N to 100 ml H_2O). On dilution with the water some diantipyrylphenylmethane separates out from the filtrate, but a test for $[Fe(CN)_6]^{3-}$ by the formation of Turnbull's blue is negative. The precipitate is dried to constant weight at 100-120° for 2 hours; sometimes some clinkering occurs but this does not affect the accuracy of the result. Similar determinations were made with different amounts of $K_3[Fe(CN)_6]$. Results of some the determinations are given in Table 1.

TABLE 1

$K_3[Fe(CN)_6]$ taken		Water, in ml	2% Alcohol solution of (II) in ml	Ppt. (II) obtained, in g	$K_3[Fe(CN)_6]$ found, in g	Expt. error, g
Solution, in ml	Weight, in g					
5	0.0250	7	12	0.1194	0.0245	-0.0005
5	0.0250	7	12	0.1210	0.0248	-0.0002
10	0.0500	15	25	0.2408	0.0494	-0.0006
10	0.0500	15	25	0.2446	0.0520	+0.0020

These results show clearly that the method is applicable to the gravimetric determination of $K_3[Fe(CN)_6]$.

b. The gravimetric determination of $K_3[Fe(CN)_6]$ in the presence of $K_4[Fe(CN)_6]$. To an accurately measured volume of $K_3[Fe(CN)_6]$ of known concentration a solution of $K_4[Fe(CN)_6]$ is added, and the determination carried out by the method described, the amount of water added being decreased by the amount of $K_4[Fe(CN)_6]$ solution used, so that the final solution still contains 50% alcohol.

Results of the determinations are given in table 2.

TABLE 2

$K_3[Fe(CN)_6]$ taken		$K_4[Fe(CN)_6]$ taken		Ppt. II obtained, in g	$K_3[Fe(CN)_6]$ found, in g	Exptl. error, in g
Solution, in ml	Content, in g	Solution, in ml	Content, in g			
5	0.0250	5	0.025	0.1212	0.0248	-0.0002
5	0.0250	5	0.025	0,1210	0.0248	-0.0002
5	0.0250	10	0.05	0.1256	0.0257	+0.0007
5	0.0250	10	0.05	0.1270	0.0260	+0.0010
10	0.0500	10	0.05	0.2456	0.0503	+0.0003
10	0.0500	10	0.05	0.2420	0.0496	-0.0004

c. Gravimetric determination of $K_4[Fe(CN)_6]$. An accurately know volume of $K_4[Fe(CN)_6]$ solution of definite concentration and containing a few drops of 2N H_2SO_4 is oxidized with 0.1 N $KMnO_4$. The $K_3[Fe(CN)_6]$ formed by this oxidation is precipitated with diantipyrylphenylmethane by the method described above.

Results are given in Table 3.

TABLE 3

$K_4[Fe(CN)_6]$ taken		Precipitate (II) obtained, in g	$K_4[Fe(CN)_6]$ found, in g	Experimental error, in g
Solution, in ml	Content, in g			
5	0.0250	0.1080	0.0247	-0.0003
5	0.0250	0.1069	0.0245	-0.0005
10	0.0500	0.2198	0.0504	+0.0004
10	0.0500	0.2610	0.0495	-0.0005

d. Determination of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ when present together. $K_3[Fe(CN)_6]$ is determined in one aliquot as described above and then another aliquot is taken which is preliminarily oxidized with 0.1 N $KMnO_4$ and the total $K_3[Fe(CN)_6]$ determined; $K_4[Fe(CN)_6]$ can then be determined by difference.

Results of these determinations are given in Table 4. For simplification only the total salts expressed as $[Fe(CN)_6]^{3-}$ are given.

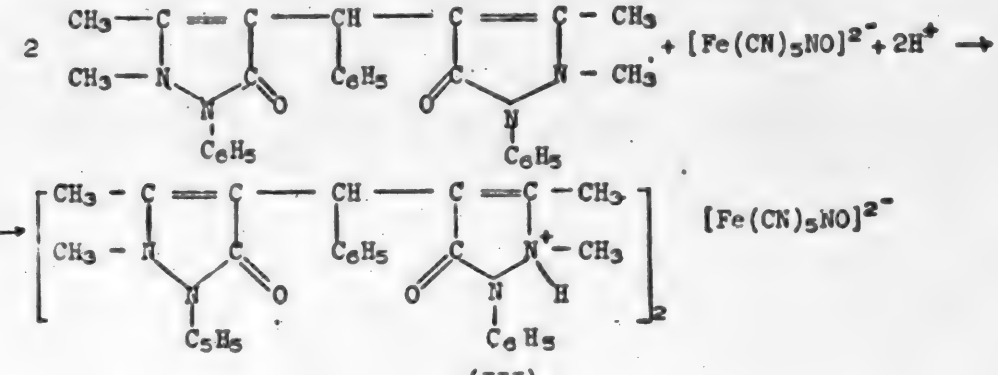
By means of diantipyrylphenylmethane, therefore, it is possible to carry out gravimetric determinations of small amounts of ferro and ferricyanides either separately or together. Attemps at a volumetric method gave high and inconsistent results.

TABLE 4

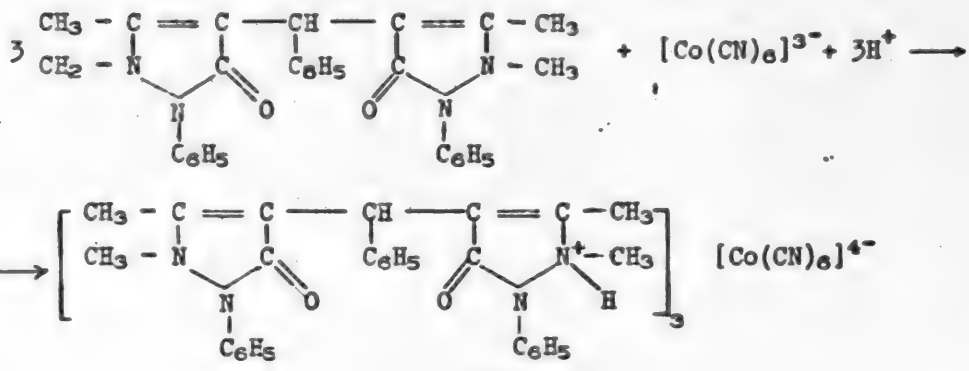
$K_3[Fe(CN)_6]$		$K_4[Fe(CN)_6]$		Ppt. obtained, in g	$[Fe(CN)_6]^{3-}$ found, in g	$[Fe(CN)_6]^{3-}$ calc. theoretical, in g
Solution, in ml	Content, in g	Solution, in ml	Content, in g			
1	0.0050	4	0.0200	0.1134	0.0149	0.0147
1	0.0050	4	0.0200	0.1173	0.0152	0.0147
2	0.0100	5	0.0250	0.1489	0.0201	0.0208
2	0.0100	5	0.0250	0.1467	0.0198	0.0208
3	0.0150	5	0.0250	0.1780	0.0235	0.0241
3	0.0150	5	0.0250	0.1814	0.0239	0.0241
5	0.0250	5	0.0250	0.2420	0.0319	0.0305
5	0.0250	5	0.0250	0.2359	0.0308	0.0305

Interactions Between The Nitroprussside $[Fe(CN)_5NO]^{2-}$ And Cobaltocyanide $[Co(CN)_6]^{3-}$ Anions With Diantipyrylphenylmethane

The reactions between these anions and diantipyrylphenylmethane proceed in the same way as for $[Fe(CN)_6]^{3-}$, i.e., with the formation of " ammonia" salts of the respective acids and base (I):



(III)



(IV)

The reaction between $Na[Fe(CN)_5NO]\cdot 2H_2O$ and diantipyrylphenylmethane (preparation of compound III). To 60 ml of a 2% alcoholic solution of diantipyrylphenylmethane diluted with 40 ml of water, and 0.5 ml of 1 N HCl, is gradually added a solution of 0.2 g nitroprusside in 10 ml water. A white bulky crystalline precipitate forms, which after filtration is washed with 21% aqueous alcohol and dried to constant weight. No $[Fe(CN)_5NO]^{2-}$ anions were detected in the filtrate (acetone test). The compound is a white crystalline material, reminiscent in form of the crystals of complex (II) under the microscope. The complex contains three molecules of water of crystallization. At 180° the anhydrous product decomposes with swelling.

Analysis of the compound formed

Weight taken in g	Weight of products obtained in g	Found Percent
0.1206	CO_2 – 0.2397	C – 65.78
0.1115	CO_2 – 0.2715	C – 65.85
0.1206	H_2O – 0.0555	H – 5.15
0.1115	H_2O – 0.0493	H – 4.90
0.7125	Fe_2O_3 – 0.0478	Fe – 4.69
0.6842	Fe_2O_3 – 0.0465	Fe – 4.75

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2[Fe(CN)_5NO]$. Calculated C – 65.96%; H – 5.09% Fe – 4.87%.

0.7964 g was taken for the determination of the water of crystallization 0.7714 g was obtained after drying.

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2[Fe(CN)_5NO]\cdot 3H_2O$. Found percent: H_2O 3.14. Calculated percent: H_2O 3.25.

The reaction between $Na_3[Co(CN)_6]$ and diantipyrylphenylmethane (preparation of compound (IV)). To 150 ml of a 1% solution of diantipyrylphenylmethane in 50% aqueous alcohol with 5 drops of 1 N H_2SO_4 is added a weak acid solution of 0.7 g of $Na_3[Co(CN)_6]$ in 25 ml water. The precipitate is washed with 25% aqueous alcohol and dried to constant weight. The complex is white crystals; under the microscope long fine needles are observed. The product contains 14 molecules of water of crystallization, after removal of which by heating, it acquires a rose color.

Analysis of the compound formed

Weight taken, in g	Weight of products obtained, in g		Found Percent	
0.1084	CO_2	0.2749	C	69.21
0.1236	CO_2	0.3132	C	69.14
0.1084	H_2O	0.0514	H	5.31
0.1236	H_2O	0.0592	H	5.36
0.6894	Co_3O_4	0.0337	Co	3.59
0.4604	Co_3O_4	0.0218	Co	3.52

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Co(CN)_6]$. Calculated C - 69.34%, H - 5.44%, Co - 3.66%.

Determination of water of crystallization.

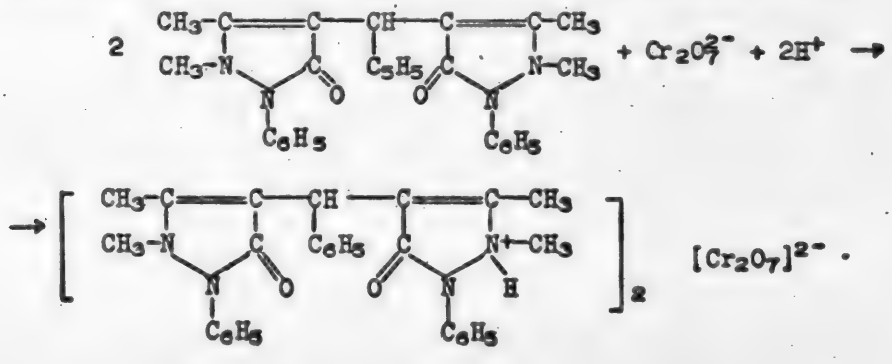
0.2016 g on drying gave 0.1740 anhydrous product.

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Co(CN)_6]\cdot 14H_2O$. Found percent H_2O - 13.71. Calculated percent H_2O - 13.5.

A precipitate can be formed by the interaction of diantipyrylphenylmethane with sodium cobaltinitrite $Na_3[Co(NO_2)_6]$. The composition of the complex formed corresponds approximately to the formula $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Co(NO_2)_6]$; it changes with time however.

The Interaction of Diantipyrylphenylmethane with $Cr_2O_7^{2-}$ and CrO_4^{2-} Ions

The formation of well formed crystalline precipitates as the result of the interaction of organic compounds with salts of sexivalent chromium is rare. The reaction therefore between $Cr_2O_7^{2-}$ (or CrO_4^{2-}) and diantipyrylphenylmethane in a weak acid medium is of interest as it leads to the formation of a yellow crystalline precipitate of the composition $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2Cr_2O_7$.



To 100 ml of a 2% solution of diantipyrylphenylmethane in 50% aqueous alcohol is slowly added about 30 ml of a 0.5 N solution of $K_2Cr_2O_7$; yellow crystals separate out, which are filtered off, washed with water and dried in a desiccator. The crystal form is shown in the photograph, Fig. 2. (See Plate, page 291)

This compound easily acquires an orange-red color, particularly if gently heated; at 100° the product is converted into a black sintered mass. The compound is only slightly soluble in water (0.06%), ether (0.02%), but is considerably more soluble in alcohol (0.9%).

Analysis of the compound formed

Wt. taken, in g	Wt. of products obtained, in g	Found percent
0.1938	Cr_2O_3 0.0262	Cr 9.23
0.2474	Cr_2O_3 0.0336	Cr 9.28
0.1278	8.68 ml 0.1 N H_2SO_4	N 9.51
0.1310	8.68 ml 0.1 N H_2SO_4	N 9.28

For $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2[Cr_2O_7]$. Calculated Cr 9.08%, N 9.55%.

No precipitate is formed by the interaction of diantipyrylphenylmethane with K_2CrO_4. Acidification of the solution with dilute sulfuric acid leads to a slow precipitation of a crystalline precipitate of the same composition as given by $Cr_2O_7^{2-}$.

In conclusion we should like to observe that diantipyrylphenylmethane can form a series of compounds which can find applications in analytical chemistry; e.g., the compound formed with cobalt thiocyanate, with zinc thiocyanate, and others, the investigation of which will be the object of further communications.

At the present time we are studying the possible applications in analytical chemistry of the reaction products of antipyrine with certain aldehydes apart from benzaldehyde, e.g. with salicylaldehyde, paradimethylaminobenzaldehyde, etc.

SUMMARY

1. By the interaction of diantipyrylphenylmethane (I) with $[Fe(CN)_6]^{3-}$, $[Fe(CN)_5NO]^{2-}$, $[Co(CN)_6]^{3-}$ and $[Cr_2O_7]^{2-}$ ions, the compounds (II), (III), (IV) and (V) are formed.

2. A method for the gravimetric determinations of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ ions either separately or together has been worked out.

The determination is made on the basis of a compound of the composition $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3H_3[Fe(CN)_6]$.

The factor for converting to $[Fe(CN)_6]^{3-}$ is 0.1319.

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A COLOR REACTION FOR THE RARE-EARTH ELEMENTS

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A number of color reactions for the rare-earth elements are either described or mentioned in the literature. Both group reactions and reactions for individual rare-earth elements have been described. Of the group reactions mention may be made of those involving aluminon [16], murexide [1a], pyrogallol or gallic acid [9], and various others.

Color reactions for individual rare-earth elements which have been described are: for cerium – those based on the oxidizing [6,7,15] or chromophoric action of quadrivalent cerium [9, 23,]; for ytterbium – those using the exceptionally strong reducing action of bivalent ytterbium [2] and for europium the strong reducing action of bivalent europium [3]; for lanthanum – reactions with iodine, acetates and ammonia [5]; for scandium – reactions with o-aminophenylarsinic acid + salicylaldehyde [19] and with murexide [1a].

Wenger and Duckert have published results of their critical study of reagents for cerium [12], rare earths and yttrium [13] and for scandium [14].

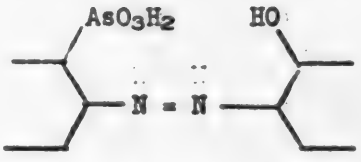
Old methods are still used alongside the new reactions for determination of the rare-earths, e.g., Hildebrand and Lendel in their textbook [17] recommend detection of the rare earths by precipitation as oxalates or fluorides despite the fact that this method is not sensitive enough, and also requires considerable time.

Group reactions for the rare-earths which have been described are only of low selectivity, and convenient methods of eliminating interference from other elements have not been worked out for these reactions. Reactions for individual elements are of basic interest for the detection of these elements in their mixtures. These reactions in the majority of cases are complex to carry out, and moreover they are not known for all the rare-earths.

In spite, therefore, of an apparent sufficiency of known reactions, the detection of the rare-earths in minerals and in the presence of other elements still presents difficulties. In this connection, the author considers that the group color reaction for the rare earth elements described in this article may be of interest.

The new color reaction is not selective; however interference on the part of other elements can be easily eliminated by simple methods which are described, while the confirmatory reaction also described guarantees freedom from errors in making wrong diagnoses on the rare earth elements.

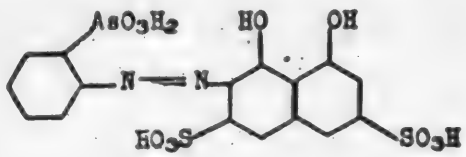
It has been shown previously [18] that compounds which incorporate the atomic grouping:



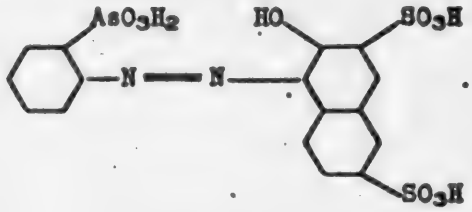
can give color reactions with the rare earth elements, and also with zirconium, thorium, and other elements.

Of reagents of this group mention may be made of o-arsonobenzene <1-azo-2> -2-hydroxynaphthalene-3,6-disulfonic acid (thoron) which has been recommended prevously for color reactions [20] and the colorimetric determination

of thorium [11,23] and of o-arsonobenzene- <1-azo-2> - 1,8 dihydroxynaphthalene-3,6-disulfonic acid which we shall call arsenazo: [1]



Arsenazo



Thoron

In the present article we shall describe a color reaction with arsenazo.

Mechanism of the color reaction. A cylic complex salt is formed during reaction with arsenazo in which there is sufficient intramolecular dissociation for determining the color observed [21].

The ionic state of the reagent which exists in solutions of this reagent in concentrated sulfuric acid ("azo-salt" + blue-violet color) and the ionic state which exists in alkaline solutions (phenolates – bluish-rose color) participate in the red-violet color of the solutions of complexes of the rare earth elements with arsenazo.

The Color Reactions of the Reagent Arsenazo

Solutions of arsenazo alone in neutral and in weak acid solutions are of a rose color, while in alkaline solution they are bluish-rose.

The rare-earth elements, Sc and Y form reddish-violet colors in neutral media. Under these conditions the following elements also give color reactions:

U^{VI} – blue coloration
Cu^{II} – blue-violet coloration
Al, V^{IV}, Th[18] – violet coloration or precipitate
Zr^{IV}, Ga, In, Pd^{II} – bluish-rose coloration or precipitate
Fe^{III} – brown lilac coloration

In addition large amounts of Ti^{IV} and Cr^{III} give violet precipitates particularly on heating. Nb and Ta also give violet precipitates under different conditions (arsenazo is added to an alkaline solution of niobates or tantalates and the mixture subsequently acidified).

Detection of the Rare Earth Elements in Pure Solutions and a Confirmatory Reaction

The rare earth elements form red-violet colors only in a neutral medium. In acid and even in weakly acid solutions no reaction occurs.

The optimum pH is ca. 7.2 (bluish-green for bromothymol blue), but reactions can be carried out in the pH range 6.5-7.5 (from yellow-green to greenish-blue for bromothymol blue).

Since the substances introduced into the usual buffer solutions in order to get the requisite pH values mask the rare earth elements, the optimum pH is produced by means of urotropine.

Detection is carried out as follows.

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[1] The synthesis of arsenazo is described at the end of this article. The synthesis of thoron has been described in [20] and in addition is included in Kulberg's book [24].

To 2 ml of test solution with an acidity no greater than 0.05 N HCl are added 1-2 drops of a 0.05% aqueous solution of arsenazo. If the solution is neutral then it is necessary to acidify it before addition of arsenazo by addition of 5 drops of 0.1 N HCl.

The absence of any change in the rose color of the reagent indicates the absence of iron, zirconium and thorium.

Next 5-10 drops of a 25% solution of urotropine are added. If only 5 μg of a rare earth element is present a red-violet color develops, which immediately changes to a rose color on addition of a few drops of 1% sodium phosphate solution. (Confirmatory test, distinction from Al, Cu, V^{IV}, Zr and partially from Th).

This slow disappearance of color after addition of sodium phosphate is characteristic for the rare-earth elements. The colors formed by other elements either do not change as a result of adding phosphate or only change slowly. If more than 5μg of a rare-earth element is present a greater amount of arsenazo can be used to increase the definition of the reaction.
For detection of the rare-earth elements in very dilute solutions it is necessary to establish the required pH value more accurately.

This is done as follows. The neutral or weak acid test solution is divided into two, to one half is added bromothymol blue and then simultaneously and equal number of drops of a 25% solution of urotropine is added to both halves until the half with the bromothymol blue acquires a bluish-green color. At this point addition of urotropine is stopped and the arsenazo is added to the half free from bromothymol blue. At high dilutions it is necessary to compare with the color of a blank.

The limiting dilution is greater than 1:3,000,000. When the optimum pH value is very carefully prepared it is possible to go as low as 1:5,000,000, but the sensitivity falls off sharply for even small deviations from the optimum pH.

The limit of identification is 0.4μg of a rare earth element (in 1 ml at a dilution of 1:2,500,000)

Fluorides, phosphates, tungstates, oxalates, citrates, tartrates, and other complex-forming compounds interfere with the color reaction because they form weakly dissociated complexes with the rare earth elements. Salicylates exhibit a slight effect.

In order to carry out the reaction by a drop technique, a drop of 0.2-0.3% solution of arsenazo is placed on filter paper and dried. The stain is touched with the end of a very fine hair capillary with a diameter of 0.2 mm and a micro drop of the test solution with the requisite pH value slowly allowed to form.

If rare-earth elements are present, then at the point of contact a violet or blue spot with diffuse edges is formed; in the absence of rare earth elements as a result of washing out of the reagent – a white spot is formed.

The limiting dilution is 1:30,000.

The limit of identification is 0.03μg of a rare earth element (in a 0.001 ml microdrop at a dilution of 30,000).

It must be emphasized that in carrying out the reaction by a drop technique, the sensitivity is very strongly dependent on the method employed. The sensitivity is greater the finer the end of the capillary and the slower the microdrop is allowed to form.

Detection of Rare-Earth Elements in the Presence of Other Elements

The direct detection of rare-earth elements is possible without any auxiliary procedures in the presence of considerable amounts of the following elements: Li, K, Na, NH_4^+: Ag, Ca, Sr, Ba, Mg, Zn, Cd, Hg^{II}, Sn^{IV}, Pb, V^V, Mo, Co, Ni and also in the presence of all anions which do not mask the rare earth elements (Cl^-, Br^-, I^-, ClO_4^-, SO_4^{2-}, $S_2O_3^{2-}$, NO_3^-). Phosphates, pyrophosphates, fluorides and tungstates mask the rare-earth elements and the reaction is not possible when these are present.

By adopting special masking methods, the rare-earth elements can be detected even in the presence of certain elements which themselves give a color reaction. Thus the detection of the rare-earth elements is possible in the presence of:

Al, Cu – on addition of salicylates
Cu – " " " $Na_2S_2O_3$
U – " " " H_2O_2

Detection of the Rare-Earth Elements in the Presence of Iron

The color reaction does not work in the presence of iron Fe^{III}. If iron is present in amounts of only 10-15 times that of the rare earth elements, detection is still possible after reduction of Fe^{III} to Fe^{II} by ascorbic acid. But in this case the color formed is of a different shade and quickly disappears, since under these conditions the Fe^{II} reaction leads to a break down of the reagent.

Small amounts of iron up to one milligram can be conveniently removed by extraction in the form of the 8-hydroxyquinolate. At the same time small amounts of aluminum are removed. This separation is effected as follows.

2-3 ml of the neutral test solutions are acidified with 4-5 drops of 0.1 N HCl and 1-2 drops of a 0.05% solution of arsenazo introduced. The mixture is shaken with 2 ml of a 1% solution of 8-hydroxyquinoline in benzene. Pure benzene may be used and a small crystal of 8-hydroxyquinoline added to it in a test tube.

The extracted iron colors the benzene a dirty green color. If the color formed is too intense, the upper benzene layer is removed with a capillary fitted with a rubber bulb and the extraction repeated with a fresh portion of a benzene solution of 8-hydroxyquinoline. When the color finally developed is not too intense, the benzene layer is removed, fresh benzene is added, and 6-8 drops of a 25% solution of urotropine added to the test solution, and the mixture shaken after the addition of each drop. When 1-2 drops have been added it is useful to remove the benzene layer and replace it with fresh. The benzene layer is carefully removed with a capillary and the lower aqueous layer is washed a few times with pure benzene, the benzene being removed after each wash. This procedure is repeated until the benzene remains completely colorless.

In the presence of rare earth elements the lower aqueous layer is colored violet but this changes instantly to a rose color on addition of sodium phosphate.

By this method it is possible to determine 1-2 μg of a rare earth element in 2 ml for a Fe^{III} content of 50 μg and 30 μg aluminum in the original solution.

It is more convenient to remove large amounts of iron by extraction with amyl-acetate [21] and not with 8-hydroxyquinoline or the method using stannic chloride described below. The procedure is as follows.

The test solution is evaporated to dryness in a test tube. If the test tube is heated on a gas burner, it should be shaken to prevent the contents spluttering, and in order to facilitate removal of condensed vapor on the sides of the test tube, air can be blown into the tube by means of a bent tube at intervals.

The residue is dissolved in 1-2 ml of HCl, Sp. gr. 1.18-1.19, 1-2 ml amylacetate is added, and the mixture shaken vigorously. The upper yellow layer containing the extracted iron is carefully removed with a capillary. If the lower acid layer has an appreciable yellow color, the extraction is repeated with fresh portions of amylacetate. For an amount of iron 100 times more than the rare earth elements one extraction is sufficient.

The acid residue is transferred to a small beaker and evaporated to dryness on a water bath. The residue is dissolved in water and the reaction for the rare-earth elements carried out as described above, separating, if necessary the remaining traces of iron and aluminum by extraction with 8-hydroxyquinoline.

Separation of the Rare-Earth Elements from Other Elements

If the amount of the interfering elements - titanium, zirconium, thorium - is not too great in comparison with the amount of rare-earth elements present, the easily hydrolyzable cations of all these elements can be removed simultaneously by co-precipitation with stannic acid, which is precipitated on hydrolysis of $SnCl_4$. This method is included below in the description of the method of detecting rare earth elements in minerals. Iron is also precipitated with stannic acid, but aluminum is not.

The Colorimetric Determination of the Rare-Earth Elements

The reaction described is also suitable for the quantitative colorimetric determination of the rare earth elements in pure solutions or in the presence of non-interfering elements. The scale method may be used (standard series method). Or the method of colorimetric titration, since the color develops slowly.

In the test solution the reagent should of course be in excess of the rare earth elements. Therefore the solution to be determined colorimetrically should have a red-violet (violet + rose) and not a violet color.

Since the individual rare earth elements for identical pH values give somewhat different colors, the individual rare earth elements in the standard solutions should be in the same proportions as in the test sample. When working with pure individual elements these complications do not apply.

As an example we describe the determination of neodymium. 3 ml of the test solution containing 1-10 μg of neodymium is introduced into a test tube and 0.2 ml of 0.1 N HCl and 0.2 ml of a 25% solution of urotropine added. A 0.01% aqueous solution of arsenazo is then added from a microburette until the violet color which is first formed changes into a distinct red-violet color. Into a second test tube exactly the same amount of arsenazo is introduced from the microburette, (important) and a volume of water slightly less than that of the test solution, the same amount of HCl and urotorpine respectively also added. This mixture is titrated with a standard solution of neodymium containing 10 μg/ml Nd from a microburette until the color obtained is the same as that of the solution in the first test tube. The volumes of the solutions are then equalized with water.

This procedure for the colorimetric determination of rare earth elements is carried out more quickly than the method recommended in the literature, according to which the rare-earth element is first precipitated as a phosphate and the phosphorus then determined colorimetrically by the molybdate method [1].

Detection of Rare Earth Elements in Minerals

Since the greatest difficulties encountered are those arising from the presence of large amounts of aluminum, it is recommended that the test object be freed mechanically as much as possible from the minerals rich in aluminum. This procedure is however not compulsory, since the confirmatory test with sodium phosphate ensures freedom from detecting a rare earth element where it does not occur.

Procedure. A grain of the mineral from 1-10 mg in weight is carefully crushed in an agate mortar, mixed with sodium carbonate, and portions fused either on the

loop of a platinum wire or on the lid of a platinum crucible. The melt is dissolved in water acidified with HCl, and a few more drops HCl added and the solution evaporated almost to dryness.

The residue is either diluted with HCl, Sp. gr. 1.18-1.19, or with water, according to whether or not it is proposed to use amylacetate for extraction of the iron. If an extraction is performed the residue is diluted with water after almost complete evaporation of the HCl on the water bath.

The amount of water taken should be such that the concentration of aluminum is not more than ca. 0.15 μg/ml of the element. By addition, if necessary, of a sodium bicarbonate solution, the solution is made slightly acid to congo red (incomplete blueing of congo red paper). 1-2 drops of a 60% aqueous solution of $SnCl_4$ are then added, and the mixture heated to boiling, and filtered from the precipitated meta-stannic acid.

If all the thorium has been completely removed, on addition to part of the filtrate of a drop of the arsenazo solution no violet color should develop; if thorium is present the separation with $SnCl_4$ is repeated in a less acid solution. When small amounts of the rare earth elements are present, the filtrate is either neutralized with ammonia or left weakly acid.

To 2 ml of the filtrate are added 1-2 drops of a 0.05% solution of arsenazo followed by 8 drops of ammonium salicylate*) solution and 1-1.5 ml of a 25% solution of urotropine.

If rare-earth elements are present a red-violet color developes which slowly changes to a rose color on addition of a few drops of 1% $Na_2HPO_4 \cdot 12H_2O$. In the absence of rare-earth elements the test remains a rose color.

When detecting very small amounts of the rare earth elements it is useful to split the solution obtained between two test tubes and to add sodium phosphate to one and compare the color shades thus obtained.

In the presence of uranium, blue solutions are formed. In this case the blue color can be destroyed by addition of H_2O_2, taking care not to add excess.

The limiting dilution of the rare-earth elements calculated as oxides in the filtrate from (meta)-stannic acid is 1:800,000. The limiting ratio

$$(\text{rare earth})_2O_3 : Al_2O_3 = 1 : 170.$$

Particles of monazite or orthite which are practically invisible to the naked eye give a definite reaction for rare-earth elements.

Synthesis of Arsenazo - o-Arsonobenzene-<1-azo-2>-1,8-dihydroxynaphthalene-3,6-disulfonic acid (sodium salt)

2.17 g of o-aminophenylarsonic acid (0.01 mol) is dissolved in 40 ml water and 3 ml HCl, sp gr. 1.12, added. The mixture is cooled and then diazotized by addition of 5 ml of 2N $NaNO_2$. The solution of the diazo compound is filtered off and poured into a cooled, filtered, solution of 4.3 g pure chromotropic acid (free from H-acid) and 4 g anhdyrous sodium carbonate in 20 ml water. After standing for 2 hours an excess of HCl, sp. gr. 1.19, is added and the dark red-brown precipitate filtered off, washed with 3 ml of HCl, sp. gr. 1.12, and recrystallized from a small volume of water. It is air dried. Yield of recrystallized product is ca. 4 g of a dark red powder.

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*) 10 g salicylic acid is shaken up with 50 ml of water and carefully neutralized with ammonia and the solution made up to 100 ml with water.

The o-nitrophenylarsonic acid necessary for the above synthesis is obtained by reduction of o-nitrophenylarsonic acid by $FeSO_4$ (or better $FeCl_2$)+ NaOH [4]. o-Nitrophenylarsonic acid is prepared by Barth's reaction from diazotized o-nitraniline and alkaline arsenite solution [10].

SUMMARY

The reagent arsenazo (o-arsonobenzene-<1-azo-2>-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Na-salt) dissolves in water giving a rose colored solution. With rare earth elements in neutral solution arsenazo forms red-violet colors which enable these elements to be detected at dilutions down to 1 : 3,000,000.

The detection of the rare earth elements in their pure solutions is described together with methods for eliminating interference from iron and other elements which react with arsenazo.

A method is described for detecting the rare earth elements in minerals, in which part of the interfering elements are separated by coprecipitation with precipitated meta stannic acid formed by the hydrolysis of $SnCl_4$, while any interfering elements remaining in solution are masked by means of ammonium salicylate.

The synthesis of the reagent is described.

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DETECTION OF CERTAIN RARE EARTH ELEMENTS WHEN PRESENT TOGETHER

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The close similarity between the chemical properties of the rare-earth elements is known to be a result of the identical structure of the two outer electron shells. An atom of one of the rare-earth elements differs from an atom of another only in the number of electrons in the 4f level. As a result up to the present characteristic reactions for the detection of the ions of individual rare-earth elements have been practically unknown. More or less specific reactions have only been described for ions of cerium, lanthanum and europium [1]. In this connection therefore a search for chemical methods for the detection of individual rare-earth elements in the presence of others is extremely desirable and of very great practical importance. The considerable experience which has been accumulated on this question, although not yielding any positive results, has led to the conclusion that the normal methods of qualitative analysis cannot be effective in the analytical chemistry of the rare earth elements.

The method proposed by us consists in converting the test compounds of the rare-earth elements into oxides and studying the interactions of these oxides with solutions of specially selected reagents. This leads to a considerable increase in the specificity, since the properties of the ions of the rare-earth elements are usually more like each other than the properties of their compounds of the same type (e.g. compare the ions of Nd^{3+} and La^{3+} and the oxides Nd_2O_3 and La_2O_3; the oxides differ essentially from each other in their basicity). In addition the possibility arises of using, for analytical purposes, compounds containing the rare-earth elements in valency states which in practice do not exist in solution (e.g. the higher oxides of praseodymium).

Detection of Lanthanum in the Presence of Other Rare Earth Elements and Other Elements Similar To It

On calcining, the carbonates, oxalates, and nitrates of other rare-earth elements and also of yttrium and thorium form oxides with weak acid properties and the two elements nearest to lanthanum - cerium and praseodymium - behave similarly. lanthanum is the only element which forms a strongly basic oxide, La_2O_3. Experiment shows that indicators with a transition interval in the pH range 6.4-10, change their colors sharply in the presence of La_2O_3, but remain practically unchanged in the presence of the oxides of other rare-earth elements. The most suitable indicator is phenolsulfophthaleïn (phenol-red) with a transition pH interval at 6.4-9. The yellow color of the indicator changes to a bright red in the presence of La_2O_3. This indicator enables 0.1 g of La (III) (after evaporation of 0.1 ml of a solution of lanthanum nitrate with subsequent calcining) to be detected at a limiting dilution of 1:1,000,000. This method under the experimental conditions used is strictly specific and enables lanthanum to be detected in the presence of cerium, praseodymium, neodymium, thorium, scandium and yttrium for a ratio of La:Me of 1:10,000 where Me is Ce, Pr, Nd. In the detection of small amounts of lanthanum in the presence of excess neodymium it is necessary to remember that neodymium oxide, after a period of 1-2 minutes, colors the reaction solution

an orange-rose color. In this case, therefore, 1-3 drops of acetone are added. If only 0.01% of lanthanum is present the color persists. In the absence of lanthanum (or when the amount of lanthanum is less than 0.01%) the color changes to the initial yellow. The role of acetone consists in lowering the sensitivity of the reagent to hydroxyl ions [4]. Only strong bases such as magnesium oxide and calcium oxide interfere with the reaction.

Procedure

Preparation of Reagent. 10 mg of phenol red is dissolved in 2 ml warm alcohol and 8 ml water added. The solution is stable.

The reaction. A few milligrams of the test sample or mixture of rare-earth salts (nitrates, oxalates, carbonates, double-ammonium nitrate salts, oxides, etc.) are placed on a platinum spoon or microbeaker and calcined in the flame of a gas burner for 1-2 minutes at a temperature of ca. 800° (when testing a solution it is preliminarily carefully evaporated). After cooling, the oxides which remain are transferred to one of the depressions on a porcelain drop test plate (for small amounts of test sample the reaction can be carried out directly in the vessel in which calcining is carried out) and a drop of the reagent added and mixed with a glass rod. If lanthanum is present, the yellow color of the reagent immediately turns red or rose. In doubtful cases 2-3 drops of acetone are added and mixed in. If no lanthanum is present the solution becomes yellow again. If a large amount of praseodymium is present it is convenient to make observation by means of a magnifying glass.

Detection of Cerium in the Presence of Other Rare Earth Elements and of Thorium Oxide

The reaction which we propose for cerium is based on the oxidation of phenylanthranilic acid, which is used in cerimetry as an oxidation-reduction indicator [5], by cerium dioxide. According to our observations it is possible to detect 0.001 μg of Ce (IV) at a limiting dilution of 1:1,000,000 by the appearance of a violet color. Since calcined cerium dioxide reacts sufficiently rapidly with the reagent, it seems to be a very suitable method for detecting traces of cerium. This reaction enables 0.001% CeO_2 to be detected in thorium oxide and also in the oxides of neodymium, lanthanum, and in other rare earth elements. The detection of cerium in the presence of praseodymium presents some difficulties, since salts of praseodymium decompose on calcining, forming higher oxides, chiefly PrO_2. The latter is a strong oxidizing agent like CeO_2 but though it does not oxidize phenylanthranilic acid as rapidly as CeO_2 it still interferes with the detection of cerium. This interference on the part of PrO_2 can be easily eliminated, if before the test the mixture of oxides is heated slightly with dilute sufuric acid when the PrO_2 forms $Pr_2(SO_4)_3$ while CeO_2 remains unchanged; in this way 0.001% of cerium can be detected in praseodymium preparations.

This reaction for Ce is characterized not only by a considerable sensitivity but also by its high specificity. Only strong oxidizing agents which are capable of oxidizing phenylanthranilic acid in a sulfuric acid medium interfere with the reaction.

Procedure

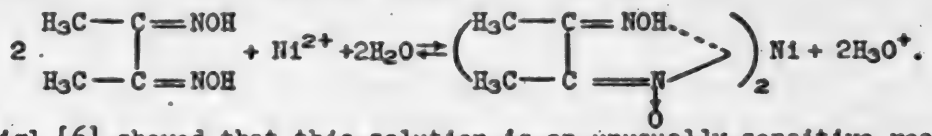
Preparation of reagent. 6 mg of phenylanthranilic acid is dissolved in 10 ml of a 0.1% solution of sodium carbonate.

The reaction. Thorium oxide and the oxides of the rare earth elements (with the exception of preparations containing praseodymium) are tested directly. Carbonates, oxalates, nitrates, double ammonium and magnesium nitrate salts are tested after preliminary calcining in a platinum spoon or in a micro beaker in the flame of a gas burner for 1-2 minutes at ca. 800°. On cooling, a few grains of the oxides formed (for testing a fraction of a milligram is enough) are placed in one of the depressions on a drop test plate, where 4 drops of H_2SO_4 (ρ = 1.84)

and a drop of phenylanthranilic acid solution have been placed beforehand. Immediately after mixing or 1-2 minutes afterwards, a violet color develops. If praseodymium is present, 1-2 drops of H_2SO_4 are added to the almost cooled, calcined oxides on the platinum spoon (on which calcining is carried out) and the mixture slightly warmed. The reaction between PrO_2 and H_2SO_4 is very rapid and its completion is established by the disappearance of the original black or dark color of the oxides. After this treatment the contents of the spoon are transferred to one of the depressions on the drop test plate and the procedure described above subsequently followed.

Detection of Neodymium in the Presence of Praseodymium and Derium

When the nitrates, oxalates and carbonates of cerium, praseodymium and neodymium are calcined, CeO_2, PrO_2 and Nd_2O_3 respectively are formed of which only Nd_2O_3 possesses any appreciable basic properties. This can serve as a basis for developing a method of detecting neodymium in the presence of praseodymium and cerium by means of the equilibrium solution formed by the interaction of dimethylglyoxime with a nickel salt in a neutral medium.



Feigl [6] showed that this solution is an unusually sensitive reagent for compounds possessing basic properties; in the presence of basic compounds a red precipitate of nickel dimethylglyoxime is formed as a result of the neutralization or adsorption of the hydroxonium ions and subsequent displacement of the equilibrium to the right. The low solubility of the substance with basic properties does not hinder the course of the reaction. Neodymium oxide reacts immediately on contact with the equilibrium solution with the formation of nickel dimethylglyoxime. Praseodymium dioxide reacts with the equilibrium solutions very slowly and it is only after 7-10 minutes that the first signs of a reaction begin to appear. Since the praseodymium compound at our disposal contains traces of neodymium (spectrographic analysis) we could not decide conclusively whether the slow appearance of the effect of the reaction is the result of the presence of these traces of neodymium or whether in fact there is a slow reaction between PrO_2 and the equilibrium solution. CeO_2 does not react with the equilibrium solution even on standing for many hours.

TABLE 1

Time necessary for the appearance of a color on the interaction of the reagent with praseodymium dioxide containing traces of neodymium oxide

Content of nedoymium in the praseodymium compound in percent	Time for color to appear in minutes
10-3	a few seconds
1	0.5
0.1	2
0.01	3
Control (praseodymium containing traces of neodymium)	7 (more clearly 15)

The sensitivity of this reaction is very high—even a grain of Nd_2O_3 practically invisible to the naked eye gives an immediate positive reaction. It is possible to detect 0.01% neodymium in preparations of cerium or praseodymium by this method. The rate at which the red nickel dimethylglyoxime appears, up to

a certain extent characterizes the quantity of neodymium in praseodymium preparations (Table 1).

It is obvious that the reaction just described is reliable only in the absence of materials of a basic character. Lanthanum oxide and the oxides of the rare earth elements up to Er_2O_3 interfere.

The succesful use of this reaction depends on scrupulous accuracy since even traces of compounds of a basic character give rise to a positive reaction.

Procedure

Preparation of reagent. 10 ml of a 4% solution of nickel nitrate is mixed with 20 ml of a 1% alcoholic solution of dimethylglyoxime, heated for 5 minutes on a water bath and filtered. In well covered flasks of inert glass the reagent keeps for 1-2 weeks. If a precipitate forms during storage it should be filtered off.

Reaction. The reaction is carried out in special micro tubes made from inert glass (or pyrex) and fitted with a ground glass stopper, (see diagram). Before test the tube is washed out with sulfuric acid then carefully with distilled water and rinsed with neutral alcohol and dried. A few milligrams of the test sample (oxalate, nitrate, carbonate, double ammonium nitrate salt but not the double magnesium salt with nitrate) are placed on a platinum spoon or microbeaker and mixed with a micro-drop of a 0.01% solution of chromium nitrate (traces of chromium according to Ryabchikov and Terentev [7] help the complete conversion of praseodymium to the higher oxides). The test sample is at first carefully and then more strongly heated in the flame of a gas burner with a blowpipe or jet (ca. 800° but not more than 900°). After cooling the oxides obtained are transferred by means of a micro funnel into the micro test tube to which 3-5 drops of reagent are added by means of a capillary. The ground glass stopper is inserted and observation made of any changes which occur, the tube being periodically shaken. Observations are made with a magnifying glass with a magnification of 5-10. The appearance of rose crystals after an interval of not more than 3 minutes, directly on the surface of the solid phase and also floating on the liquid indicates the presence of neodymium in the test sample of praseodymium or cerium (when other compounds of a basic character are know to be absent).

4/5 actual size

When preparations of cerium or praseodymium thoroughly purified from foreign materials are tested, as a rule one need not be apprehensive of mistakes connected with the presence of the substances indicated (i.e. compounds of a basic character).

Detection of Praseodymium in the Presence of Neodymium, Cerium, and Other Rare Earth Elements

The black product formed on calcining the nitrate or oxalate of praseodymium [8] according to some results corresponds to the empirical formula Pr_6O_{11}, while according to others [9] it corresponds to PrO_2. In contrast to CeO_2, this black product is fairly soluble in acids forming the respective salts of trivalent praseodymium. The nitrate and oxalate of neodymium on calcining in air form the normal oxide Nd_2O_3. The existence of the higher oxide of neodymium NdO_2 which apparently is formed on calcining of the oxalate in an oxygen atmosphere is doubtful [9].

The oxidation-reduction potential of the system:

$$Pr(III) - \underline{e} \rightleftarrows Pr(IV)$$

is greater than 1.6 V [10].

Thus it seems possible [11] that an oxidation-reduction reaction can be used for detecting praseodymium (after conversion of the higher oxides) in the presence of neodymium.

Of a number of oraganic compounds which we have tested the most suitable as reagents for Pr(IV) were benzidene and particularly o-tolidine, which on oxidation form blue compounds [12].

If an acetic acid solution of o-tolidine is allowed to act on the higher oxides of praseodymium formed by calcining the oxalate, nitrate, or carbonate, an intense light blue or dark blue color is immediately formed, which is the result of the formation of tolidine blue. The limit of identification is 0.0 μg of Pr at a limiting dilution of 1:10,000,000.

A spectrographically pure preparation of magnesium neodymium nitrate gives a scarcely observable color (less intense than that for 0.01 μg of Pr). Neodymium preparations containing praseodymium give intense positive reactions. Thus it is possible to detect in an aliquot of magnesium neodymium nitrate containing 5 mg neodymium as little as 0.04 μg of praseodymium, corresponding to a ratio of Nd:Pr = 1:12,500.

Calcined CeO_2 when reacted with a solution of o-tolidine in acetic acid gives only a pale blue color, while the color of the solution above the precipitate remains practically unchanged (acquires a pale-greenish color). This fact, coupled with the insolubility of CeO_2 in acetic acid, enables traces of praseodymium to be detected in the presence of cerium. Thus the spectrographically pure preparation of magnesium cerium nitrate at our disposal showed a negative reaction for praseodymium, while that containing traces of praseodymium gave a definite reaction.

Ions which under the reaction conditions form higher oxides capable of dissolving in acetic acid and in such a solution oxidizing the o-tolidine, interfere with the detection of praseodymium.

Of the other rare earth elements only terbium is capable of giving a similar reaction, since its compounds on calcining form Tb_4O_7, in which terbium is found partially in the quadrivalent state. Nevertheless Tb_4O_7 in contrast to PrO_2 at elevated temperatures is unstable and completely decomposes at 800° in a nitrogen atmosphere, being converted into colorless Tb_2O_3 [9]. Unfortunately we did not have any terbium compound at our disposal so that we coule not test its effect on the reaction which we have suggested for praseodymium.

Procedure

Preparation of reagent. 0.02 g of o-tolidine is dissolved in 1 ml 60% acetic acid by slight heating and 2 ml of 1 N sodium acetate added. If any turbidity develops a few drops of acetone are added to clarify the solution. The reagent is stable and should not acquire a blue color on storing in a stoppered dark flask.

The reaction. The reaction can be carried out with either the dry test mixture - oxalates, nitrates, carbonates, the double ammonium and magnesium salts, or with their solutions. A few milligrams of the dry mixture or a corresponding number of drops of the test solution are placed in a platinum spoon or microbeaker and at first carefully heated, then in the course of 0.5-1 minute the mixture is calcined at a red heat in the flame of a gas burner (temperature of 800° but not more 900°). After cooling 2-3 drops of reagent solution are placed on the spoon. If praseodymium is present then a more or less intensive blue or pale blue color develops both on the liquid and solid phase either immediately or within a few seconds. If the test sample of cerium or neodymium does not contain praseodymium, then only the solid phase is colored blue, while the liquid above the solid remains colorless or has a hardly observable greenish color. A blank test with distilled water or with spectrographically pure preparations of the rare earth elements is essential only when a very pale blue color is obtained, indicating vanishingly small amounts of praseodymium in the test sample.

SUMMARY

A method has been developed for the detection of lanthanum, cerium, and praseodymium in the presence of other rare earth elements, and the detection of neodymium in the presence of praseodymium and cerium. Phenol red is the reagent used to detect lanthanum, phenylanthranilic acid for cerium, and equilibrium solution of nickel dimethylglyoxime for neodymium, and o-tolidine for praseodymium.

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THE REACTION BETWEEN THE BISMUTH ION AND BENZIDENE

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Benzidene, which was synthesized by N.N.Zinnin in 1845, has been widely used during the last 50 years both in analytical chemistry and also for the syntheses of dyes [1] and a number of other compounds.

Feigl [2] by means of benzidene detected the ions of Cu, Pb, Au, Cr, Mn, Tl, Ce, F, CN, CNS, S_2O_8, SiO_4, and Tananaev [3] in addition detected [SiF_6-], NO_2- and Cl- ions.

The capacity of benzidene to give with certain acids very slightly soluble salts has been adopted for the determination of sulfuric [4], tungstic [5], and phosphoric acids [6], respectively.

In 1930, Tugarinov [7], while studying the possibility of using organic reagents for the qualitative detection of cations, briefly described a reaction between bismuth salts, benzidene and potassium iodide. The absence in the work mentioned of any detailed results characterizing the compound formed prompted us to attempt to fill this gap.

When a crystal of potassium iodide is added to a clear and not very dilute solution of a bismuth salt until the precipitate originally formed dissolves, then as a result of the formation of $[BiI_4]^-$ ions the liquid acquires a bright yellow color. Greater amounts of potassium iodide lead to the formation of $[BiI_5]^{2-}$ ions and the appearance of an orange-yellow color. On addition of a solution of benzidene hydrochloride to the liquid thus obtained, a golden-yellow or bright red precipitate forms immediately. If liquid and precipitate are heated to a temperature not exceeding 75° the golden-yellow crystals dissolve and bright red crystals settle out on cooling. Increasing the acid concentration favors the reverse process, but in the presence of concentrated acid the reaction ceases altogether. Use of a microscope facilitates the detection of bismuth in small amounts of liquid. In a drop of 0.01 N $Bi(NO_3)_3$ in the cold, golden-yellow crystals, of irregular, needle-like form, appear after 1-3 minutes, while in a drop of 0.004 $Bi(NO_3)_3$ containing 0.014 mg of the Bi ion, crystals can be observed after 3-5 minutes.

The crystals may have different forms. During rapid crystalization from a hot solution, bright red rhombohedra are formed, which in time dissolve and are replaced by more or less regularly shaped parallellepiped and needles (Fig. 1; see plate, page 291) . Slow crystallization leads to the formation of irregular needle-shaped crystals (Fig. 2, Plate). Under favorable condition of growth their length attains 1 cm.

For the study of the properties and composition of these crystals they were prepared as follows: to a clear, concentrated solution of bismuth chloride was added crystalline potassium iodide until an orange-yellow color was formed. To the clear liquid thus prepared was added a solution of benzidene hydrochloride (excess of the latter should be avoided). The liquid and precipitate which was formed were heated on a water bath to a temperature not greater than 75°. If the transition of the yellow crystals into the red is not fast enough, then an

additional amount of potassium iodide can be added. On rapid cooling of the heated solution by means of cold water, fine crystals separated out, which, after removal from the liquid, were dried between sheets of filter paper. If crystals of benzidene are detected in the preparation the precipitate is recrystallized under the same conditions of temperature in a small volume of liquid containing the $[BiI_5]^{2-}$ ion. If the air-dried crystals are allowed to stand for a long time in the open in bright sunlight there occurs a gradual change in the color to a chocolate brown. This same brown color also develops with time if the crystals are exposed to the ultraviolet from a quartz lamp. The color of the precipitate underneath the surface of the mother liquor or the color of the dry precipitate in a closed vessel in the dark does not change in the course of many months.

No solvent has been found for the precipitate. It is completely insoluble in hot and cold water, ethyl alcohol, chloroform, carbon tetrachloride and acetone. It hydrolyzes in water.

Concentrated acids and alkalis rapidly destroy the red crystals. Hydrochloric acid favors a change of the color of the crystals to yellow. Concentrated nitric acid at first preserves the external form of the crystals, but changes their color initially to black, which eventually changes to brown. At the same time elemental iodine is formed. Hot nitric acid causes a rapid break down of the substance, with simultaneous separation of violet iodine fumes. Concentrated sulfuric acid destroys the substance, with the formation of a dark powdery mass and colorless tablets of benzidene sulfate. The action of caustic alkalis forms a white amorphous precipitate, while aqueous ammonia gives a yellow precipitate. Gaseous ammonia slowly changes the red color of the crystals to a lemon-yellow.

Elevated temperatures have the following effects: above 78° the crystals gradually begin to loose their bright red color and acquire a brown color, which in its turn becomes chocolate brown. Intensive decomposition sets in at 241°. Crystals dried at 150-190° on slow cooling absorb moisture from the air and regain their original red color. This type of change can be repeated several times on one lot of crystals. On moistening freshly dried crystals by breathing on them, it is possible to observe the restoration of the original bright red color in the course of a few minutes.

The air dried powder was analyzed to determine its composition. Iodine was determined as follows: 0.15-0.25 g was treated in an excess of standard $AgNO_3$, and 1 ml of indicator - a nitric acid solution of ferric sulfate - added at the same time. The red crystals were immediately destroyed, with the formation of silver iodide. The liquid and precipitate were left to stand until all the dark particles disappeared. To accelerate the reaction, the particles were broken up with a glass rod. After 20-40 minutes, twice its volume of water was added to the liquid and precipitate, and the excess silver back titrated with ammonium thiocyanate. The equivalence point was determined not only by the indicator, but also by the appearance of a grey color in the precipitate.

Bismuth was determined as the oxide. 0.2-0.3 g of the compound was treated with excess concentrated nitric acid and heated slightly. After removal of the iodine as vapor the weak nitric acid solution was diluted with water, and, after addition of ammonium carbonate, the bismuth in the precipitate was determined gravimetrically. Water was determined by taking 0.3 g of the air-dried material in a beaker and keeping it in a drying oven at a temperature of 150-155°. When drying was finished, the beaker was immediately closed with a ground glass stopper and cooled in a desiccator over P_2O_5. Under these conditions the dry chocolate-brown precipitate changed its color only very slightly, as a result of absorption of moisture during weighing. Benzidene was determined by difference.

The results are given in the table.

TABLE

	Found in, separate determinations		Average %	
Iodine	59.42	59.57	59.59	59.53
Bismuth	19.62	19.72	19.58	19.64
Water	3.49	3.47	3.51	3.49
Benzidene (by difference)		-	-	17.34

The analytical results lead to the following formula for the red crystals: $H_2N \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2 \cdot H_2[BiI_5] \cdot 2H_2O$.

Thus, the compound is a benzidene salt of pentaiodobismuthic acid with two molecules of water of crystallization.

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DETERMINATION OF MINIMAL QUANTITIES OF ARSENIC IN ORGANIC COMPOUNDS BY MEANS OF BIVALENT CHROMIUM SOLUTION

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Having considered the complexity and awakwardness of the methods recommended for the determination of arsenic in organic compounds [1,2] we decided to determine arsenic by means of a solution of bivalent chromium. The presence of antimony and other contaminants should not affect the accuracy of the determination.

As our experiments have shown, antimony ions are reduced by bivalent chromium in a neutral medium, while arsenic (V) is reduced in acid media. In acid media arsenic is reduced by bivalent chromium to metallic arsenic, which is filtered off and determined iodometrically. The reaction proceeds according to the following equations.

1. $As^{5+} + 5Cr^{2+} \longrightarrow As^{0} + 5Cr^{3+}$.

2. $2As^{\circ} + 5I_2 + 8H_2O \rightleftarrows 2AsO_4^{3-} + 10I^- + 16H^+$

   $(NaHCO_3) \qquad HCO_3^- + HOH \rightleftarrows H_2CO_3 + OH^-$

$NaHCO_3$ is added to prevent reduction of arsenic acid to arsenous acid by the action of iodine ions.

The arsenic content is calculated from the following formula:

$$As = \frac{N_I(V_1 - V_2)\cdot 74.91}{1000\cdot 5} \text{ in grams,}$$

where V_1 is the total amount of iodine in ml; V_2 is the excess of iodine solution in ml; 74.91/5 is gram-equiv. of As.

For the determination of arsenic in urine, the latter is acidified with HCl (30% by vol) and an excess of bivalent chromium solution added in a stream of CO_2. Quinquevalent arsenic is reduced to the elemental state on heating to 100°.

The arsenic which separates out is filtered off, and washed with 5% NH_4Cl until a neutral reaction is obtained. The precipitate and filter paper (paper pulp can be used for rapid filtration instead of filter paper) are transferred to a flask fitted with a ground glass stopper, and 10-15 ml of a 2% solution of $NaHCO_3$ plus a known volume of standard iodine solution added. The excess iodine is back-titrated after 5-10 minute against sodium arsenite or sodium thiosulfate.

Results of determinations are given in Table 1.

TABLE.

As taken, in g	As found, in g	As taken, in g	As found, in g
0.002	0.002	0.0006	0.0006
0.002	0.002	0.0006	0.0006
0.0068	0.0068	0.0006	0.0006
0.0036	0.0036	0.0006	0.0006
0.0036	0.0036	0.0006	0.0006
0.0068	0.0068	0.0006	0.0006

These results on the determination of arsenic introduced into urine as sodium arsenite show that arsenic (V) can be determined in amounts of 0.5 mg/liter In organic compounds (neosalvarsan) arsenic is determined as follows.

An aliquot of the organic compound (neosalvarsan) is decomposed with concentrated nitric acid (sp.gr.1.4) in the presence of 2% $KMnO_4$ (the decomposition is repeated). On cooling, a concentrated solution of sulfuric acid is added, and the solution heated till the appearance of white fumes. When this solution is cold, water is added and then HCl (30% by volume of the solution). An excess of a solution of bivalent chromium is added in a stream of CO_2 and the whole heated to 100°. The metallic arsenic is then treated as described above. Results are given in Table 2.

For the determination of arsenic in urine, the daily (24 hour) urine of a patient is concentrated to a volume of 100-200 ml, and is treated with HNO_3 (sp.gr.1.4) in the presence of 2% $KMnO_4$ (10 ml).

The solution is evaporated to a volume of 80 ml and subjected to oxidation until it stops frothing.

The nitrates are converted into sulfates. Arsenic is then determined in the light yellow, clear solution as described above.

TABLE 2

As taken, in g	As found, in g
0.0038	0.0037
0.0038	0.0037
0.0019	0.0019
0.0019	0.0019
0.0019	0.0018
0.0019	0.0020
0.0019	0.0018

Arsenic in amounts of 0.5 mg/liter can be determined.

This method of determining arsenic (in urine) which has been developed for clinical laboratories can also be used in forensic laboratories.

The Cr^{1+} solution used can be prepared by the author's electrolytic method [3,4] or by Popov's method [5].

SUMMARY

A rapid and accurate method has been developed for the determination of arsenic in organic compounds (in urine and neosalvarsan) based on the reduction of arsenic to the elemental stage by a solution of bivalent chromium.

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A METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF COPPER

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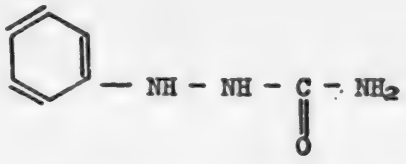
Phenylsemicarbazide, C_6H_5-NH-NH-CO-NH_2, reacts with copper salts to form yellow or red colors according to the amount of copper. The color obtained changes instantaneously to a golden yellow on the addition of an ammonia solution. The formation of this yellow color is a highly sensitive reaction and has been used by us for the colorimetric determination of copper as described below.

Colorimetric comparison is made by means of standard solutions with a constant relative difference between the concentrations of adjacent solutions in test tubes of thin colorless glass. The diameter of the test tube is 0.9 cm, the height of the solution in the test tube 7 cm and the volume 5 ml.

Characteristics of the New Method For The Colorimetric Determination of Copper

Phenylsemicarbazide is mentioned in the literature as a medicine under the patent name "cryogenin" [2], while in other literature sources the name "tryogenin" is applied to metabenzamidosemicarbazide [4,5]:



Phenylsemicarbazide

Metabenzamidosemicarbazide

An aqueous solution containing 0.1 g of phenylsemicarbazide in 100 ml water is used as the reagent [1].

We adopted the following order for carrying out the reaction: 0.6 ml of

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1) Synthesis of phenylsemicarbazide: 28.8 g of phenylhydroazine hydrochloride and 18 g of urea are carefully mixed and ground in a porcelain mortar and the mixture placed in a round bottomed flask. It is then heated at 150-160° for 4-6 hours on an oil bath [6]. The melt after cooling is ground and worked up with 300-350 ml distilled water heated to the boil. The hot solution is immediately filtered. The precipitate which separates after cooling is sucked free of mother liquor, rapidly, and washed with cold water after which it is recrystallized twice from alcohol. The final product is dried in a vacuum desiccator over calcium chloride. The pure compound melts at 171°.

the reagent is added to ca. 4 ml of test solution and the volume made up to 5 ml. To increase the rate of the reaction the test tube may be immersed in boiling water. The contents of the test tube should be heated to 91-92°, after which they are cooled and a drop of 10% ammonia solution added. When this is done the weak yellow or rose color changes immediately into a golden yellow color.

The reaction is fairly specific. The majority of colorless cations do not interfere. The most suitable concentration range for the colorimetric determination of copper is 0.025–5 μg in 5 ml (Table 1).

TABLE 1

Conc of copper in μg/5ml; height of layer in test tube 7 cm.		Difference in conc. between adjacent solutions, in percent	Number of standards	Observations
From	To			
0.01		–	–	Gives a color which is already different from that of the blank.
0.01	0.015	30	2	
0.015	0.25	20	3	
0.025	5	10	55	
0.17	0.3	5	11	
5	8	20	4	
8	12	30	4	
	>12	No difference		

The curve for the absorption[1] of light is shown in Fig. 1

The high value for $\log \varepsilon$ (~5) in the region of maximum absorption confirms the high sensitivity of this reaction.

The yellow color obeys the Buger-Beer law for certain concentration ranges of copper (Fig. 2).

The highest color intensity develops when the neutral or very weak acid solution of copper is heated with reagent (before addition of ammonia).

Large amounts of other salts NH_4Cl, NH_4NO_3, $NaNO_3$, NaCl, Na_2SO_4 and K_2SO_4 lower the color intensity; their effect becomes perceptible when their ratio to copper becomes 10,000 mol/mol copper. Nitrates have a smaller effect than chlorides and sulfates.

During the determination of very small amounts of copper (of the order of a microgram and fractions of a microgram), we came up against losses of copper as a

Fig. 1 Light absorption curve for copper solutions containing 0.2 μg of copper/ml; cell length 5 cm.
1) Measurements made immediately after heating, 2) measurements made after 24 hours.

1) A spectrophotometer of the Konig-Martens type was used. The apparatus was kindly lent by the Kharkov Sci. Research Institute of Metrology and Standardization.

result of adsorption on the surfaces of the flasks used. The following special experiments were accordingly carried out; a copper solution was placed in a porcelain basin and evaporated to dryness, the dry residue was worked up with 3 drops of nitric acid and again evaporated to dryness, then extracted 3 times with 1 ml lots of water; the extracts were all collected in one test tube; to this mixture 0.6 ml of reagent was added; the total volume was made up to 5 ml and the solution heated and ammonia added. These experiments showed that at low copper concentrations, the copper could be recovered practically completely after such a treatment. But on increasing the amount of copper the relative amounts of copper recovered decreased (Table 2).

By extracting the copper with hot water, followed by prolonged heating, low results were obtained (Table 2), possibly as a result of hydrolysis of copper salts.

A threefold extraction with cold water, in which the water was allowed to stay in contact with the dry residue for 10 minutes after addition of each lot, gave satisfactory results at low concentration and improved the results at high concentrations. Increasing the duration of the water treatment to 20 minutes

TABLE 2

Copper taken in μg	Copper found in μg					
	Nitrate	Sulfate	Acetate	Extraction with prolonged heating	Extraction with cold water on standing	
					10 min	20 min
0.12	0.10	0.10	0.12	0.05	0.12	0.14
0.24	0.13	0.18	0.19	0.06	0.24	0.27
0.48	0.25	0.24	0.37	0.09	0.37	0.50
0.96	-	-	-	-	0.67	0.99

made it possible to determine large amounts of copper satisfactorily (Table 2). New, unused porcelain basins even under the best conditions do not completely give up their copper. After repeated determinations in the same basins their surfaces become gradually saturated with copper, the amounts of copper determined increase and finally approach the normal values (Table 3, Columns 1,2).

The method of cleaning the surfaces of the beakers before determining the copper is very important. By very vigorous treatment, e.g., immersion in nitric acid (1:4) and boiling, the surfaces are completely freed from copper and start to adsorb copper again when they are used for subsequent determinations, until the surface becomes saturated (Table 3, Columns 3,4,5).

It was found that constant results could be obtained by the following method of cleaning; 1-2 ml of concentrated nitric acid is placed in the basin and heated on the water bath (2-3 minutes until fumes appear), the acid at this stage is not at a temperature greater than 60°, the acid is poured off and the beaker rinsed several times with water. This operation is repeated three times.

The results of experiments which characterize the losses of copper as the result of adsorption are given in Table 3.

Gurevich [8] observed a similar behavior for the adsorption of lead by the surfaces of flasks.

In 1933 Sarata proposed a colorimetric method for the determination of copper by means of metabenzamidosemicarbazide in the presence of lead acetate [3,4]. On heating, the copper solution with this mixture for 40-50 minutes at 40°, a red color develops which can be used for colorimetric determination.

According to Sarata, 0.5 to 30 μg of copper can be determined by this method.

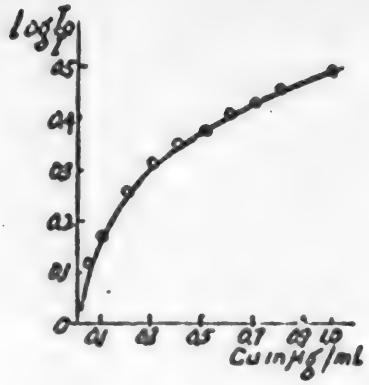


Fig. 2 Curve for the optical density of copper solutions of different concentrations. Determinations were made at a wave length of 4960 A; cell length 1 cm.

In so far as phenylsemicarbazide also gives a similar reaction with copper salts, we investigated the conditions for the colorimetric determination of copper by means of the red color; the latter appears under the conditions given above in the absence of lead acetate as well, but it is not so intense. The intensity and shade of the red color is strongly dependent on the ratio between the amount of copper and reagent. The greatest intensity for the red color is observed for a ratio of 1 mol copper to 12 mols of reagent. With increasing concentration of lead acetate the color intensity increases up to a ratio of 1 mol copper to 10 mols lead acetate. Further increase in the amount of lead decreases the intensity.

The curves for the absorption of light in copper solutions containing 0.2 μg/ml for a constant ratio between the amount of copper and phenylsemicarbazide (1 mol copper to 12 mols reagent) and for different amounts of lead acetate are given in Fig. 3.

TABLE 3

Copper taken in γ g	Copper determined in γ g				
	New basins		Old basins, cleaned by boiling in nitric acid		
	1	2	3	4	5
0.12	0.10	0.10	0.10	0.10	0.11
0.24	0.13	0.18	0.13	0.16	0.22
0.48	0.18	0.40	0.21	0.36	0.44
0.96	0.54	0.78	0.52	0.74	–

Fig. 3 Light absorption curves for different concentrations of lead acetate: 1) 1 mol; 2) 10 mols and 3) 14 mols.

The value of log ε in the region of maximum absorption indicates the lower sensitivity of the given reaction in comparison with the reaction which we have proposed. This is confirmed by the results on the concentration limits of copper which are most suitable for colorimetric determination according to the red color (Table 4).

The necessity of observing a definite ratio between the amount of copper and the reagent in order to get comparable colors requires a knowledge of the approximate content of copper in the test sample. This is a big drawback and limits the practical application of the method.

The method which we have proposed involving the use of phenylsemicarbazide, and based on the formation of the golden-yellow color after heating and addition of ammonia, is free of these drawbacks and is twenty times more sensitive than Sarata's method [4].

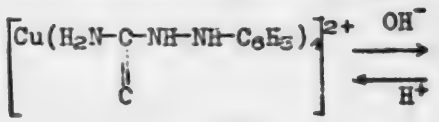
In order to elucidate the nature of the colored product formed, solutions of the product were electrolyzed.

During electrolysis of the red solutions obtained by heating a solution of a copper salt with phenylsemicarbazide in the course of 40 minutes to 40°, a transfer of the red color to the cathode immersed in agar-agar is observed. A similar transfer of the red color to the agar-agar during the time of experiment was not observed in a control test. On repeating the experiment with the yellow solution, penetration of the yellow color into the agar-agar layer was observed in the case when the electrode immersed in the agar-agar was made the anode. Consequently, the red color of the solution is determined by the presence of red cations, and the yellow color by yellow anions, The composition of the yellow complex was investigated spectrophotometrically by Job's method [7]. As a result the curve depicted in Fig. 4 was obtained.

TABLE 4

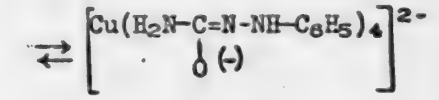
Concentration of copper in μg/5ml (height of layer 7 cm)	Difference in concentration between adjacent solutions percent	Number of standards	Observations
1	–	–	Gives a color already distinguishable from blank
From 1 to 2	20	4	
2 to 22	10	23	
22 and higher	>10	–	

On the basis of what has been said we suggest that the structure of the red and colored compounds is analogous to the ammine complex of copper



(I)

Red Cation (neutral media)



(II)

Yellow anion (alkaline media)

The copper in these complexes can hold the phenylsemicarbazide by means of the (free) pairs of electrons of the NH_2 group. It is well known that these groups determine the basic properties of phenylsemicarbazide.

Doubly charged cations with a red color(I) can be formed in a neutral medium. In an alkaline medium the stability of complex (I) is apparently maintained, but favorable conditions are created for the enolization of four carbonyl groups. As a result a doubly charged anion with a yellow color is formed with the probable structure (II).

Determination of copper in blood

Blood was chosen for testing the method developed, first because it is one of the difficult objects in analysis and secondly because the development of a method capable of wide application for the determination of copper in blood would be very useful for clinical purposes.

Even the most sensitive of known methods requires no less than 0.5-1 ml of blood. The sensitivity of our method makes it possible to decrease this volume to 0.1 ml; this is of considerable significance.

According to results in the literature, the normal content of copper in human blood amounts to 120-150 μg/100 ml. The amount of iron is more than 400 times as much.

It was demonstrated that for concentrations of iron less than 0.4 μg/5ml no color is formed with phenylsemicarbazide. For amounts of 0.5 μg and over, a pale yellow color develops which is not proportional to the iron concentration.

The following experiment showed that iron could be separated by means of hydrolysis.

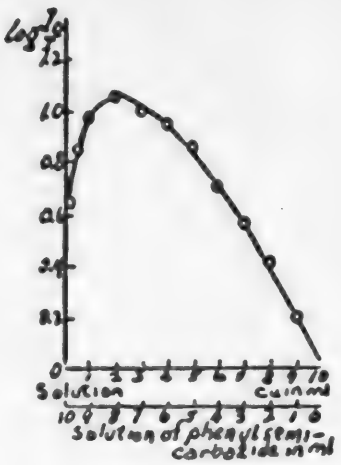


Fig. 4. Light absorption curve by Job's method. 0.001 M solutions of copper and phenylsemicarbazide were used in the experiments.

A solution containing 50 μg iron (0.1 ml of blood contains this amount of iron) was evaporated to dryness in a porcelain dish. The dry residue was treated with 3 drops of concentrated nitric acid and evaporated on a water bath, worked up with 3 drops of water, and evaporated again. The dry residue was worked up 3 times with water, (1 ml of water each time), and the volume finally made up to 5 ml. On addition of phenylsemicarbazide to the solution thus obtained, the liquid remained colorless. It is clear therefore that iron remains practically insoluble under these conditions. By separating 0.12 μg of copper and 50 μg iron in this way and subsequently determining the copper in the aqueous solution, satisfactory results were obtained (Table 5).

For the determination of copper in 0.1 ml of blood taken from the same person's finger by pricking with a needle, the residue after ignition of the blood in a muffle was worked up with nitric acid and water as described above. When this was done the copper content found in separate determinations was. 0.10, 0.18, 0.10, 0.12, 0.15, 0.15, 0.15, 0.15, 0.15, 0.15 μg of copper.

These values for the copper content of blood are in good agreement with results in the literature.

Results for the determination of copper in blood with and without the additon of a known weight of copper are given in Table 6. 0.1 ml of blood was taken for testing.

TABLE 5

Iron taken, in μg/5ml	Copper taken, in μg/5ml	Copper found, in μg	Iron taken, in μg/5ml	Copper taken, in μg/5ml	Copper found in, in μg
50	–	Colorless Solutions	–	0.12	0.10
50	–	"	50	0.12	0.15
50	–	"	50	0.12	0.10
–	0.12	0.12	50	0.12	0.10
–	0.12	0.12	50	0.12	0.10
–	0.12	0.14			

TABLE 6

Copper added, in μg	Amount of copper that should be present, in μg	Copper found, in μg	Deviation, in μg	Recovery, percent
–	–	0.12	–	–
–	–	0.12		
0.12	0.24	0.24	0	100
0.12	0.24	0.25	+0.01	105
0.24	0.36	0.34	−0.02	94
0.48	0.60	0.55	−0.05	92
0.48	0.60	0.67	+0.07	112
0.48	0.60	0.55	−0.05	92

The results in Table 6 show that it is possible to determine copper in blood by the method proposed with an error of not more than 10%.

Instructions for the Determination of Copper in Blood Reagents

a) 0.1 g of phenylsemicarbazide in 100 ml serves as the reagent. The solution

is prepared in small amounts daily since the solution starts to turn yellow 2-3 days after preparation.

b) Water. For this work water twice distilled from glass vessels is used. "Pyrex" flasks cannot be used, since it was observed that water from such flasks decreases the sensitivity of the reaction. In doubtful cases blank tests should be carried out on the water.

c) Concentrated nitric acid. If a blank test gives colored solutions then the acid should be purified by distillation.

d) 10% Ammonia solution. If a blank gives a color, then the aqueous ammonia solution should be prepared by distillation of ammonia into twice distilled water with cooling.

Apparatus. a) For ignition of blood samples porcelain dishes with unscarred enamel and not more than 5 cm in diameter should be used.

It is difficult to achieve complete ignition of organic compounds in dishes with rough surfaces. Pyrex dishes and ones of transparent quartz did not give satisfactory results in our experiments.

The dishes to be used should be tested beforehand. Standard solutions of copper should be used, the concentrations of which are similar to those of the test solutions, in order to ascertain whether or not copper is adsorbed by the dish surfaces. If the amount of the copper found is less than that taken, then it is necessary to evaporate solutions of copper of similar concentrations to the test solutions from the dishes several times.

b) Cleaning of the dishes after analysis. Most of the dry residue is removed with moist lumps of some soft material. After this treatment the dish is worked up three times with concentrated nitric acid, the contents being heated on the water bath for 2-3 minutes. After each nitric acid treatment the dish is washed with water. Dishes used for copper analysis should not be used for any other purpose.

c) The test tubes in which the colors are compared should be made of thin, colorless glass, without seams, and should have a diameter of ca. 10 mm; 5 ml of liquid should fill them to a height of not less than 7 cm. The test tubes should be stored full of distilled water. When necessary the surfaces should be cleaned by washing with nitric acid.

Preparation of Standard Solutions

500 mg of electrolytic copper is dissolved in 5 ml nitric acid, 1:1, and the solution thus prepared made up to 500 ml. Such a solution contains 1 mg/ml. Two other solutions are prepared from this primary standard, one containing 1 μg/ml and the other 0.1 μg/ml. These can be used for preparing a series of standards.

A 2 ml pipette with scale divisions of 0.01 ml is used for measuring out the standards. 5 standards (less and greater than 0.12 μg) are sufficient: 0.084, 0.12, 0.17, 0.24 and 0.34 μg copper in 5 ml.

The difference in concentration between two adjacent solutions in this series is 30%. Interpolation between these standards enables determinations to be made with an accuracy of up to 10%.

1. Blood Sampling. Test samples are taken from a finger by pricking with a needle. The blood is collected in a micropipette of 0.1 ml capacity one drop of blood should be enough for duplicates. The blood is transferred from the pipette to a dish containing 3 drops of concentrated nitric acid. The blood is immediately carefully mixed with nitric acid by a rotary motion of the dish until a uniform mixture is obtained.

2. Ignition. The contents of the dish are dried on a water bath, after which it is placed in a muffle at a dark-red heat. Complete ignition usually takes 15-20 minutes. After ignition there remains a dark, grainy residue which becomes red on cooling. A gas burner cannot be used for this ignition.

3.Extraction of copper and colorimetric determination. The residue from ignition is treated with three drops of concentrated nitric acid, dried on a water bath, then treated with three drops of water and again dried. The dish is removed from the bath, treated with 1 ml of water, and allowed to stand for 20 minutes, the dish being periodically shaken with a rotary motion. The water extraction is repeated 3 times.

To the solution poured into a test tube 0.6 ml of the phenylsemicarbazide solution is added and the volume made up to 5 ml.

The test tubes containing the test solutions and those containing the standards are immersed simultaneously in water, and heated until the contents have a temperature of 92°.

After cooling, one drop of 10% ammonia solution is added to each test tube and the contents mixed with a thin glass rod. The colors are then compared. It is possible to carry out a series of analyses simultaneously.

The present research was done under the direction of Prof. V.G.Gurevich.

SUMMARY

A new, very sensitive colorimetric method is proposed for the determination of copper. Amounts of copper as low as 0.025 μg/ml can be determined with a relative error of not more than 10%.

The method does not require the use of organic solvents.

As an illustration of its application in practice, the determination of copper in blood may be quoted. 0.1 μg of copper in 0.1 ml of blood can be determined. A method has been worked out for the separation of copper from iron.

It has been shown experimentally that the colorimetric determination of copper by means of phenylsemicarbazide in the presence of lead acetate by means of the red color developed is not very suitable as a practical method.

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Received December 14, 1949

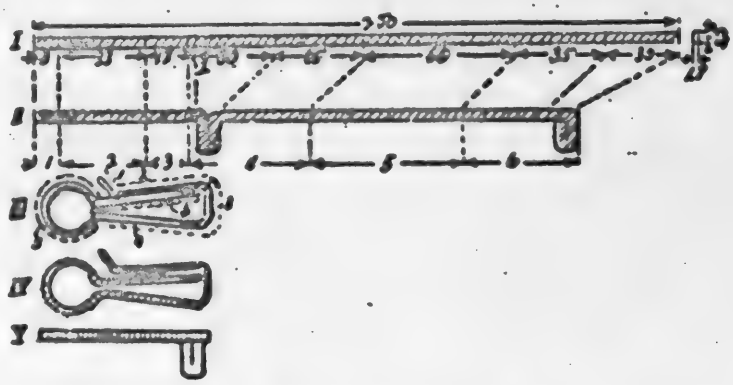
A NEW CLIP

D.M.Borinets

Clips of the Mor type are used in all chemical laboratories. This clip has certain disadvantages.

It constricts the tube on one side more than on the other. It is impossible to regulate the constrictive force of the clip according to the elasticity of the tube. It is difficult to restore the lost constrictive force of the clip. In order to fit the clip on to a tube, one end of the tube has to be free.

The new type of clip which I have designed is free from all these disadvantages of the Mor type. The method used for making one of these clips is very simple (see diagrams). Iron 3 mm wide is flattened out to give a wire of the dimensions 3.5 X 1.7 mm (I). It is then bent into shape (II) and then into (III) as shown in the diagrams. The dimensions indicated are optional. According to what tubes the clips are to be used on, the cross sections and the length of the wire may be varied. It is advisable to anneal those points on the wire where it is to be bent, before the actual bending.



Working drawings for making a clamp as constructed by Engineer D.M.Borinets.

I – 3 mm steel wire, flattened to 3.5 X 1.7 mm;
II – Same wire with grips bent;
III – Finished clamp (bending scheme), top view;
IV – Clamp in use;
V – Lateral view of clamp.

Received February 4, 1952

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CHRONICLE

THE CONFERENCE ON ANALYTICAL CHEMISTRY IN GORKY

A regional conference on analytical chemistry was held from the 4th to the 6th of June in Gorky. About 260 people participated, including scientific workers from Moscow, Leningrad, Kiev, Saratov and many other towns, and also workers from the chemical industry in Gorky itself. The work of the conference which proceeded apace, apart from plenary sessions, was divided up among different sections.

Altogether 40 papers were heard

A number of reports was devoted to the theory of the action and application of organic reagents in analysis.

In V.I.Kuznetsov and L.M.Kulberg's report the effect of the structural characteristics of the molecules of an organic reagent on its reactivity was considered. In depicting the so-called characteristic atomic group, this influence was not taken into account, and consequently the presence in the molecules of different reagents of "one and the same" grouping does not always indicate similar reactions for these reagents.

I.S.Mustafin showed that a similar simplified conception exists regarding the effect of the molecular weight of a reagent on the solubility of the reaction products. Only in homologous and similar series of reagents does the solubility decrease regularly with increasing molecular weight of the reagent, the weighting effect".

The completeness of the precipitation of tungsten by organic reagents is determined by the nature of the precipitant and the state of the tungsten in solution (normal tungstates, para, meta). The most complete precipitation of all forms of tungsten is effected by salts which are not too weak basically and have a high molecular weight—alkaloids, methylene blue, methyl blue, methyl violet, rivanol, etc. (B.A.Platunov).

V.I.Kuznetsov compared colorimetric determinations with one and two colored reagents. The latter necessitate working at very precise pH values and are less selective; reagents of this type however are known for almost all the elements, and the reactions are more sensitive.

In the colorimetric determination of nickel in the presence of cobalt and other elements it is convenient to extract the nickel dioxime complexes, which in the case of difuryl- or diphenyl-dioxime are more intensely colored than the dimethylglyoxime (V.M.Peshkova). Methyl violet which gives colored solid phase reactions is used for the determination of microgram quantities of tungsten and mercury. Mercury is determined in the presence of bromides of iodides (A.F. Nemirovskaya, M.P.Ananevskaya) Mercurized analine and other amines are suitable for the microcrystalloscopic detection of a number of anions (A.A.Belyakov).

V.F.Barkovsky and L.M.Kulberg read a paper on the colorimetric determination of platinum by means of a blue color formed by chloroplatinates with acetamide. For the determination of traces of Cl, L.D.Borzova and L.M.Kulberg used the formation of intensely colored indophenols. For the colorimetric determination of boron a new reaction involving the use of azomethane dyes from H-acid and salicylaldehyde is applied. (T.I.Badeeva and L.M.Kulberg).

K.B.Yatsimirsky in his report indicated the expediency of the thermodynamic approach to the solution of various problems in analytical chemistry. A.K.Babko reported on the application of silico- and phospho-molybdic acids in analysis and the study of their compounds by the Ostromyslensky–Job method and the limitations of this method.

In the section on the polarographic and chromatographic methods reports were read by V.B.Avilov on the physico-chemical bases of the iodometric determination of As, Sb, Fe, Sn, Cr, V, and the theoretical basis of certain oxidation-reduction methods. V.F.Toropova read a report on the results of the polarogaraphic investigation of the acetate complexes of Pb and Cu which confirmed the effects of acetate buffers which have been previously observed.

A.M.Vasilev, V.F.Toropova and A.A.Busygina reported on the possibility of separating Cu, Cd, and Zn by ion exchange on Wofatit P, using solutions containing thiosulfate and acetate. V.N.Lenskaya and L.M.Kulberg studied selective reduction on ion exchange compounds. It seems that in the case of MnO_4^-, $Cr_2O_7^{2-}$ and CrO_4^{2-} ions selective reduction is observed which varies according to the experimental conditions and the nature of the ion-exchange resin.

V.P.Millin discussed the experimental and theoretical bases of electrography. M.L.Tsap reported on the photoelectric absorptiometer FA-52 which is simply constructed and can be used for the wave length range 400-1300 mμ and on the potential uses of the near infra-red for analysis.

Interesting papers were read on topochemical reactions (L.M.Kulberg) and on F.I.Flavitsky's reaction, which occurs during the pulverization of solid materials. (I.M.Isakov) (e.g., for the determination of the higher valency states of the rare-earth elements). The development of Flavitsky's reaction led to new rapid methods for diagnosing and decomposing minerals. Yu.G.Titova reported on micromethods for the determination of selenium.

Papers on sanitary-hygiene analysis were heard at the conference: the determination of tetraethyl lead in air by absorption with an alcoholic iodine solution (E.V.Gernet); the determination of silico-organic compounds in quartz in the presence of silicates, using the unequal relation of these compounds to H_6SiF_2 (S.S. Gurvits); the determination of a number of aromatic amines and phenols, by conversion into colored and fluorescent compounds (D.N.Vaskevich) et al.

The analysis of organic compounds was discussed; rapid micro-methods for the simultaneous determination of several elements (M.O.Korshum, V.A.Klimova, N.S. Sheveleva, E.G.Bereznitskaya) et al.

A number of reviews were heard at the conference; on the polarographic determination of organic compounds (I.A.Korshunov); the determination of organic sulfur compounds in gases used for catalytic synthesis (S.N.Kazarnovsky) et al.

V.I.Fuznetsov

CRITICISM AND BIBLIOGRAPHY

"Scientific Reports of Kharkov State University", Vol. 37.

"Proceedings of the Scientific-Research Institute of Chemistry", 1951, Kharkov, 170 pp. Circulation 500.

"The Collection of the Proceedings of the Scientific-Research Institute of Chemistry" contains 24 articles on different questions in analytical chemistry. N.P.Komar is either the author or one of the participants in 17 of these papers; altogether 17 chemists participated in the work reported.

The volume of the proceedings under review is not devoted to one theme, though 18 of the articles relate to various problems in colorimetric analysis, spectrophotometry, and the chemistry of colored compounds. The wide application of mathematical methods for the characterization of various equilibriums and processes of importance in analytical chemistry is a feature which is common to all the articles. Five of N.P.Komar's papers devoted to a number of fundamental problems in the colorimetric method of investigating multicomponent systems are of the greatest importance. The study of the composition and properties of colored compounds in solutions has been taken up by a number of investigators recently.

The method of physico-chemical analysis of solutions enables a number of questions which are of importance in colorimetry and in the chemistry of colored compounds to be solved. The method of equimolecular mixtures suggested by Ostromyslensky[1] and developed by Job and other investigators is of great interest for the determination of the composition of complexes in solution. In the first of Komar's articles mentioned above it is shown in a general form, that by means of this method it is not the composition of the colored complex that is determined, but only the ratio, between the coefficients of the reaction equation. Therefore in a case where one of the components participates in a side reaction, complications arise which must be taken into account.

In other articles a number of questions on the methods of determining composition, dissociation constants, and the optical characteristics are considered for the case of the formation of two colored compounds, and further in cases where the color of the reagent depends on the pH of the solution, etc.. Two articles by V.N.Tolmacheva are devoted to similar questions. In these papers a number of formulas is given which considerably facilitate the calculation of the basic characteristics of a system on the basis of the observations made.

A number of articles by the same authors and also by L.P.Adamovich and others are devoted to investigations of individual colored compounds; the quinalizarin-beryllium complex; the compounds of zinc with methylviolet and thiocyanogen, and reactions for cadmium and cobalt. All these articles are also distinguished by detailed mathematical treatment of the questions and give a series of new and important characteristics for individual reactions. The composition of the majority of the colored compounds investigated are determined as well as their optical constants and the instability constants or their equilibrium formation. The experimental part of these and other papers indicate a sound approach on this side of the investigation.

In some of the articles calculations and experimental results are given for

various questions in chemical analysis, e.g. the method of determining nitrites in the presence of nitrates, and the chromate method for the determination of sulfates, etc.. Finally, there are four articles which are included under the general heading of 'The mathematical evaluation of the sensitivity of chemical reactions". In these articles on the basis of the work of a number of investigators and by the adoption of a mathematical treatment of the results, the range for positive reactions for sulfates, iron and ammonium ions and also the effect of certain reaction conditions are evaluated.

This short review given above of the contents of the Collection shows it to be of great interest. Almost all the articles are original scientific researches. Every chemist who is interested in the question of physico-chemical analysis of solutions and also in some of the individual reactions mentioned above will find valuable material in the Collection. On the other hand the high scientific level of the work enables one to forecast a large demand for the Collection. In this connection therefore it is essential to point out a number of deficiencies.

The articles of N.P.Komar and V.I.Tolmacheva mentioned above on the optical method of investigating equilibria unfortunately give only algebraic interpretations; the geometrical method is hardly used although it is more graphic. In addition the formulas deduced are usually not written down in a "workable" form. There are no lists of symbols and sometimes, (e.g., on p. 74, etc.) there are symbols the meanings of which have to be sought for in other articles. This hinders the introduction of these formulas into practical experimentation.

The authors are often carried away by the form of the mathematical calculations. As a result the methods master the authors when it should be otherwise. In some cases detailed calculations are made in connection with certain aspects of a process which are not the basis of the method. Thus, N.P.Komar's experimental results on a method for eliminating adsorption in the chromate method of determining sulfates are undoubtedly interesting, nevertheless the results have not direct bearing on the calculation of the solubility of barium chromate in trichloroacetic acid. Meanwhile, in order to carry out the calculations actually made, a complex procedure is adopted, including extraction of activity coefficients, equations of the 5th order, and solutions involving three successive approximations. While as the result of the author's excessive faith in Landolt's tabulated results, calculations yielding results which differ by as much as three times from N.P.Komar's experimental results are made.

Sometimes the effect of non-aqueous solvents on dissociation is not taken sufficiently into account and the physical mechanisms of certain processes are not always considered correctly. Thus, L.P.Adamovich in his article on the quinalizarin-beryllium complex calculates the instability complex; in order to do this the total concentration of beryllium uncombined in the colored complex is taken as the concentration of the free beryllium ions. In a medium of 0.3 N alkali, however, the beryllium ion cannot exist in a free state. The indicator properties of quinalizarin are also not explained. Thus, in effect, it is the equilibrium constant of the reaction which is calculated and not the instability constant of the complex. This does not detract from the value of the results obtained, nevertheless the determination applies to another equilibrium.

In the study of systems involving solid phase reaction products several important factors were not taken into account. In the physico-chemical analysis of solutions, maxima and other characteristic points are observed on the property-composition diagram. Nevertheless these special points serve as a basis for making conclusions as to the composition of a compound only when there is a proportionality between the numerical values of the property considered and the concentration of the respective compound. At the same time the absorption of light by suspensions of a colored insoluble compound may depend not only on the amount of solid in unit volume of suspension, but also on the particle size of the solid. L.P.Adamovich and P.V.Starchenko in their article on the reaction between zinc and methylviolet observed this phenomenon but do not adduce any results on testing the effect. It is possible that this fact (or others) may be the reason for the rather improbable

conclusions which the authors reach, viz., that methylviolet, zinc and the thiocyanate ion are found in the ratios 6:1:4 in the complex; on this assumption it follows that a cation with four charges should be precipitated and not a neutral molecule (see equation p. 28).

It is not sufficient to use chromatographic methods for checking the purity of organic reagents. Some preparations, e.g. quinalizarin, are rarely individual compounds.

There are some editorial errors and inappropriate expressions on p. 10 "adsorption"; is used for absorption; on p. 15 there is an expression "Results in an exaggerated form;" p. 17 " complex forming compounds are decanted"; p.23 "changing competitors;" etc.

Despite these drawbacks the Collection contains very valuable material. In the articles included new and important steps are made in the development of the optical method of investigating solutions and a number of other questions in analytical chemistry. The Collection characterizes the high scientific level of Soviet analytical chemistry and the undoubted sucess of the Scientific Chemistry and the undoubted success of the Scientific Collection of the Institute.

A.K.Babko

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The Use of the Ultraviolet in Analytical Chemistry.
2. Quantitative Microchemical Analysis in the Ultraviolet. p. 221.

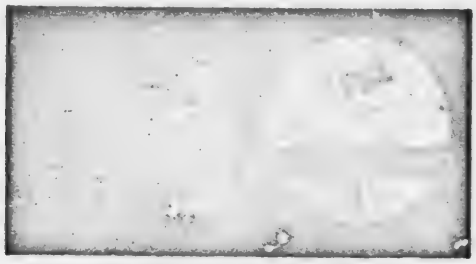

Fig. 1. Absorption spectrum and microphotograph of $PbCl_2$ and $PbBr_2$.

The Use of Diantipyrylphenylmethane in Analytical Chemistry. 2. p. 249.

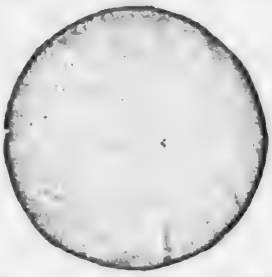

Fig. 1. Crystal form of $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_3 \cdot H_3[Fe(CN)_6] \cdot 9H_2O$. Magnification 80.

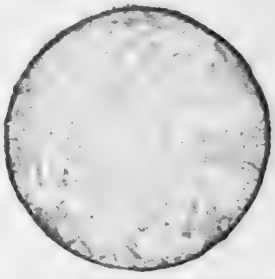

Fig. 2. Crystal form of $[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2Cr_2O_7$. Magnification 80.

The Reaction Between the Bismuth Ion and Benzidene. p. 269.

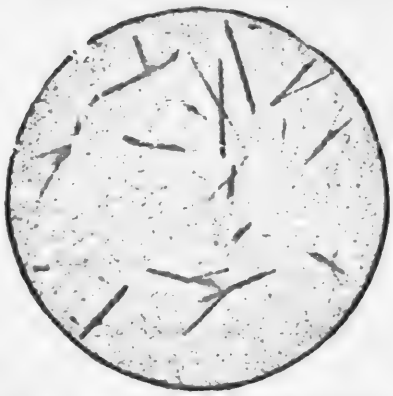

Fig. 1. Benzidene, $H_2[BiI_5] \cdot 2H_2O$. Crystallized from hot solution.

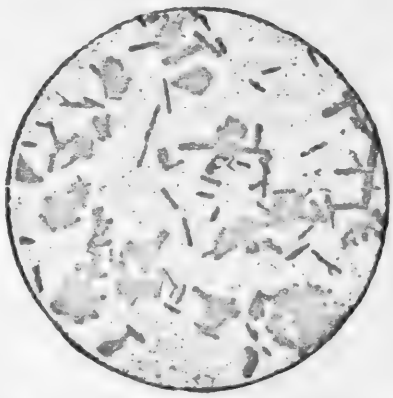

Fig. 2. Benzidene, $H_2[BiI_5] \cdot 2H_2O$. Crystallized from cold solution.

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A CRYOSCOPIC METHOD FOR THE DETERMINATION OF ARENES (AROMATIC HYDROCARBONS) IN LIGROIN, KEROSENE, AND GAS OIL PETROLEUM FRACTIONS OF STRAIGHT DISTILLATION

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A cryoscopic method which we have developed for the quantitative group determination of aromatic hydrocarbons is described in the present article. The method is based on the well known chemical thermodynamical principle that for dilute solutions, the depression of the initial crystallization temperature of a solvent is proportional to the amount of solute dissolved in it. This relation [1] can be expressed by the equation (1):

$$\Delta t = \frac{N}{A} \alpha N, \qquad (1)$$

where Δt is the depression of the initial temperature of crystallization ($t_{cryst.}$) caused by the solute; N is the percent molar concentration of the solute; A – the cryoscopic constant (the content of solute in mol. percent which gives rise to a depression of 1 deg in t_{cryst} of the solvent) which is characteristic for any given solvent; α is the depression of t_{cryst}, caused by 1 mol. percent of the solute.

It follows from equation (1) that for any given solvent the depression of its initial temperature of crystallization is proportional only to the content of the solute expressed in mol. percent, and is independent of the nature of the solute. This propoerty is used in the cryoscopic method proposed for the quantitative determination of aromatic hydrocarbons in petroleum fractions. The method is essentially as follows.

Cyclohexane is chosen as the solvent and its initial temperature of crystallization is determined. To the cyclohexane a small amount (ca.3%) of the petroleum fraction to be tested is added. The initial crystallization temperature of the cyclohexane is thereby lowered by a certain amount which is denoted by Δt_1 (e.g. 7.26°). The solution of the petroleum fraction in cyclohexane is then treated with concentrated H_2SO_4 under conditions described below. As a result of this treatment the aromatic hydrocarbons contained in the fraction originally added to the cyclohexane are removed and the total amount of the petroleum fraction contained in the cyclohexane decreases accordingly. The initial crystallization of the cyclohexane solution of the fraction will increase slightly. Let this increase be denoted Δt_2 (e.g. 1.46°):

$$7.26^\circ \ (\Delta t_1) \ 100\%,$$
$$1.46^\circ \ (\Delta t_2) \ x\%.$$

From which we find that $x = \frac{1.46 \cdot 100}{7.26} = 20.1\%$, (molar).

or the fraction treated contains 10.1% (mol) of aromatic hydrocarbons. The general form of the equation for calculating the aromatic hydrocarbon content in a test mixture on the basis of the experimental results is as follows:

$$x_{mol} = \frac{100 \cdot \Delta t_2}{\Delta t_1} \qquad (2)$$

where x_{mol} is the content of aromatic hydrocarbons in mol %; Δt_1 the depression of t_{cryst} for cyclohexane after addition of the test mixture; Δt_2 the elevation of the crystallization temperature of the solution of the test mixture in cyclohexane after the H_2SO_4 treatment.

From the example given above it is clear that for the quantitative determination of aromatic hydrocarbons by means of the cryoscopic method in the form described above, it is not necessary to weigh the cyclohexane or the fraction to be tested accurately. It is accurate enough to use a buret or pipet for adding ca.3% of the fraction or 0.3-0.5 ml according to the molecular weight. Not even a knowledge of the cryoscopic constant of the solvent is necessary.

In principle, any other individual solvent (i.e., not a mixture of solvents) can be used instead of cyclohexane as long as it does not react with H_2SO_4 and is a good solvent for petroleum fractions. Cyclohexane however has the following advantages: 1) a high value for a (1 mol % of a solute depresses the initial crystallization temperature of cyclohexane 2.42°); 2) the suitability of the value of the initial crystallization temperature (+6.55° for pure cyclohexane); and 3) it is comparatively easily available.

EXPERIMENTAL

Characterization of the Original Compounds and General Experimental Procedure

The original alkanes and cyclanes were given a preliminary treatment with 98% H_2SO_4 until there was no further change in their physical constants; they were then distilled. The original aromatic hydrocarbons did not contain more than 1.3% of alkanes or cyclanes. Petroleum fractions boiling in the ranges 150-200°, 200-250°, 250-300°, 300-350° and 350-400° were also used after removal of the aromatic hydrocarbons by adsorption on silica gel. That all the aromatic hydrocarbons had been completely removed was checked by passing the fractions repeatedly through a column packed with fresh lots of silica gel and testing their physical constants. Only in two cases (the 150-200° fraction from heavy Balakhany petroleum and the 300-350° fraction from Kalinsky petroleum) were the aromatic hydrocarbons separated by treatment with 98% H_2SO_4. All the fractions were obtained from individual petroleums. The petroleum aromatic hydrocarbons were isolated from individual petroleums by silical gel adsorption and were kindly placed at our disposal by our colleague M. S. Borova of our Institute. The properties of the original compounds are given in Table 1.

The temperature of crystallization was determined in a Beckmann apparatus used for molecular weight determinations, provided with an automatic stirrer. The temperature was measured by means of an ordinary thermometer graduated from -30 to +20° with scale divisions of 0.1°. The temperature could be read to an accuracy of 0.02° by using a magnifying glass. Since in this particular case it is a difference between points on the thermometer that has to be measured and not the absolute value of the temperature, an accuracy of the above order is sufficient. The cooling liquid used was alcohol plus solid carbon dioxide. The difference between the temperature of crystallization of any test mixture and that of the cooling bath did not exceed 1-2°.

10-15 ml of pure cyclohexane was introduced into the inner tube of the Beckmann apparatus and its initial temperature of crystallization determined. 0.3-0.5

TABLE 1

Physico-Chemical Constants of the Original Hydrocarbons and Fractions

No.	Designation of the hydrocarbons and fractions	Mol. wt.	Crystallization temp., °C	B.p. ranges at 760 mm Hg	d_4^{20}	n_D^{20}	Critical solution temp. in aniline, in °C
1	Cyclohexane	84.2[3]	+6.00	80.45-80.65	0.7787	1.4260	-
2	Diethylbenzene (mixture of isomers)	134.2[3]	-	178.2-183.9	0.8637	1.4912	-
3	Decahydronaphthalene (mixture of isomers)	138.2[3]	-	-	0.8710	1.4690	+36.9
4	Pentamethylbenzene	148.2[3]	+57.3	-	-	-	-
5	1-Methylnaphthalene	142.2[3]	-	239.0-241.0	-	1.6090	-
6	Triethylbenzene (mixture of isomers)	162.3[3]	-	216.0-218.4	0.8813	1.4989	-
7	2,6-Dimethylnaphthalene	156.2[3]	+110-110.5	216	-	-	-
8	2-Phenylheptane[1]	176.3[3]	-	230.1-230.8	-	1.4892	-
9	1,2-Diphenylpentane	182.3[3]	+50.7	-	-	-	-
10	n-Hexadecane	226.4[3]	+17.2	-	-	1.4345	+68.8
11	Diamylnaphthalene (mixture of isomers)	268.4[3]	-	-	-	1.5520	-
12	Dicyclohexylindane (mixture of isomers) $C_{21}H_{30}$[2]	282.4[3]	-	178-179 (3 mm)	1.0011	1.5510	-
13	Alkane-cyclane part of the 150-200° fraction from Bibieibatsky petroleum	136.0[4]	-	150-200	-	1.4337	+60.9
14	Alkane-cyclane part of the 150-200° fraction from Balakhany heavy petroleum	141.0[4]	-	150-200	-	-	+60.5
15	Alkane-cyclane part of the 200-250° fraction from Kalinsky Petroleum	175.0[4]	-	200-250	-	1.4520	+67.5
16	Alkane-cyclane part of the 250-300° fraction from Kalinsky Petroleum	226.0[4]	-	250-300	-	1.4600	-
17	Aromatic hydrocarbon fraction 300-350° from Buzovinsk Petroleum	233.2[4]	-	300-350	-	-	-
18	Aromatic hydrocarbon fraction 350-400° from Buzovinsk Petroleum	258.8[4]	-	350-400	-	-	-
19	Alkane-cyclane part of the 300-350° fraction from Kalinsky Petroleum	263.0[4]	-	300-350	0.8479	1.4642	+89.2
20	Alkane-cyclane part of the 350-400° fraction from Buzovinsk Petroleum	293.0[4]	-	350-400	-	-	-

1) Was synthesized by I. L. Kotlyarevsky. 2) The sample of dicyclohexylindane was kindly placed at our disposal by E. S. Pokrovska. 3) The molecular weight was calculated on the basis of an empirical formula. 4) The molecular weight was determined experimentally by a cryoscopic method using benzene.

ml of the test fraction was then added to the cyclohexane and the temperature of crystallization of the solution determined. The solution was then treated with 1 volume of concentrated H_2SO_4 in order to remove the aromatic hydrocarbons, subsequently separated from the H_2SO_4 and washed successively with 10% NaOH and H_2O till the solution was neutral. The solution was finally dried over anhydrous $CaCl_2$. The crystallization temperature for this treated solution was finally determined.

The value of α, i.e., the depression of the crystallization temperature of cyclohexane as a result of the addition of 1 mol % of different hydrocarbons was determined by measuring the crystallization temperature of cyclohexane by the method described above before and after addition of the solute in amounts of 2-3% (mol). The value of α is calculated from the experimental results by means of equation (3)

$$\alpha = \frac{\Delta t}{a} \qquad (3)$$

where α is the depression of the crystallization temperature of cyclohexane caused by addition of 1 mol % solute; Δt - the depression of the crystallization temperature of cyclohexane caused by addition of a known weight of solute; a - the amount of solute added in mol %.

Experimental Determination of the Depression of the Crystallization Temperature of Cyclohexane by Addition of 1 Mol % Solute

It was stated above during consideration of equation (1) that for any given solvent the depression of its initial temperature of crystallization is proportional only to the content of the solute expressed as molar % and is independent of its nature. In order to check this statement experimentally the values of α, i.e., the depression of the crystallization temperature of cyclohexane (used in the method proposed as the solvent) caused by addition of 1 mol.% of different solutes (Table 2), were determined.

The results in Table 2 show that hydrocarbons which have molecular weights similar to that of cyclohexane and which are similar in structure give low values for α, probably as a result of the formation of solid solutions. Thus on addition of methyl cyclohexane the value of α is 1.90 instead of the expected value of 2.42[1], i.e. 21% lower. When benzene was added to cyclohexane the value of α obtained was 2.25 which is 7.6% lower than the calculated value; the value of α obtained by using toluene was 2.34, i.e., 3.3% lower than the calculated value. Hydrocarbons such as n-hexane, and n-heptane which have similar molecular weights to cyclohexane but differ considerably in structure from it give normal values for α. All the other hydrocarbons and mixtures of hydrocarbons tested, differing in structure and with molecular weights varying from 134-291, on addition to cyclohexane depress the crystallization temperature by an average of 2.47. The mean deviation of the values found from the mean was equal to 1.1%, while the maximum deviation (in one case) was 2.8%. The deviation of the mean value of α (2.47) from the calculated value was 2%. It should be noted that errors in determining the molecular weight of a mixture of hydrocarbons by a cryoscopic method in benzene might be a contributory cause for the maximum deviation of 2.8% in one particular case. Analogous results were obtained for four determinations of the cryoscopic constant of cyclohexane when four synthetic mixtures of petroleum fractions boiling between 150-200°, and containing aromatic hydrocarbons were added to cyclohexane. These results are not included in Table 1 so as to save space. The average value of α is 2.44. It can be regarded therefore as experimentally established that the depression of the crystallization temperature of cyclohexane is proportional (with an accuracy of ±3%) to the solute content, but is independent of the nature of the solute, when mixtures of hydrocarbons which have boiling points of 150° and over are used as solutes.

[1] The value of α = 2.42 was calculated from the heat of crystallization of cyclohexane (639.3 cal/mol). For further details see [2].

TABLE 2

Depression of the Crystallization Temperature of Cyclohexane by Addition of 1 mol % of Different Hydrocarbons and Mixtures of Hydrocarbons.

No.	Composition of Mixture	Mol. wt.	Depression of $t_{cryst.}$ produced by mol % sol. deg./mol.% (α)
	Calculated on the basis of the heat of crystallization of cyclohexane.	–	2.42
1	n-Hexane	86.2[1]	2.42
2	Benzene	78.1[1]	2.25
3	n-Heptane	100.2[1]	2.45
4	Methylcyclohexane	98.2[1]	1.90
5	Methylbenzene (toluene)	92.1[1]	2.34
6	Diethylbenzene (mixture of isomers)	134.2[1]	2.48
7	A synthetic mixture of 9.4 mol.% diethylbenzene and 90.6 mol.% decahydronaphthalene	137.8[1]	2.44
8	A synthetic mixture of 82.0 mol.% n-hexane and 18.0 mol % 2-phenylheptane	217.4[1]	2.49
9	A synthetic mixture of 29.7 mol.% triethylbenzene (mixture of isomers) and 70.3 mol.% of n-hexane	207.3[1]	2.44
10	A mixture of alkanes and cyclanes, the 300-350°fraction from Kalinsky petroleum	263[2]	2.50
11	A synthetic mixture of 42.5 mol.% of aromatic hydrocarbons (300-350°fraction) and 57.5 mol.% alkanes and cyclanes (300-350°fraction) from Buzovinsky petroleum	250[2]	2.46
12	A synthetic mixture 7.7 mol.% of aromatic hydrocarbons (350-400°fraction) and 92.3 mol.% alkanes and cyclanes (350-400°fraction) from Buzovinsky petroleum.	291[2]	2.40
13	A synthetic mixture of 26.3 mol % aromatic hydrocarbons and 73.8 mol % alkanes and cyclanes (350-400°fraction) from Buzovinsky petroleum.	284[2]	2.45
14	A synthetic mixture of 49.6 mol % of aromatic hydrocarbons (350-400°fraction) from Buzovinsky petroleum and 50.4 mol % of alkanes and cyclanes (350-400°fraction) from the same petroleum.	291[2]	2.40
15	200-250°fraction synthol	176[2]	2.46
16	250-300°fraction synthol	214[2]	2.50

1) Molecular weight calculated on the basis of an empirical formula for the hydrocarbons and their content in the mixture.

2) Molecular weight determined experimentally by a cryoscopic method in benzene.

Checking the Cryoscopic Method on Synthetic Mixtures

The test mixtures as pointed out above were added in amounts of ca.3%. The aromatic hydrocarbons content in the cyclohexane therefore does not usually

exceed 1%. The low concentration of the aromatic hyrocarbons necessitates specific conditions for the H_2SO_4 treatment. It is necessary to remove this small amount of aromatic hydrocarbons completely, while the H_2SO_4 used must not react appreciably with the alkane and cyclane part of the fraction.

One of us with Kurindin [2] showed that monoalkylbenzenes with seven and more carbon atoms in the alkyl group are not completely removed by 98% H_2SO_4, fuming H_2SO_4 with a low concentration of free SO_3 being necessary. As a typical alkylbenzene which is only removed with difficulty by H_2SO_4, we chose 2-phenylheptane.

In order to establish the optimum conditions for H_2SO_4 treatment of the test mixtures in cyclohexane for the elimination of the aromatic hydrocarbons, tests on 14 synthetic mixtures were carried out. The amount of aromatic hydrocarbons in each of these mixtures was determined by the cryoscopic method described above.

Results of these tests (Table 3) showed that the majority of the aromatic hydrocarbons are completely removed by 99.0–99.5% H_2SO_4. However for complete elimination of 2-phenylheptane, fuming H_2SO_4 containing 0.2–0.3% free SO_3 was necessary. For the quantitative determination of aromatic hydrocarbons in petroleum fractions by the cryoscopic method, therefore we adopted the following H_2SO_4 treatment: 1 hour shaking by hand of equal volumes of fuming H_2SO_4 containing 0.2–0.5% free SO_3 and the cyclohexane solution.

The accuracy of the proposed cryoscopic method for the quantitative determination of aromatic hydrocarbons was tested on 40 synthetic mixtures (Table 4). The mean error was equal to 0.6% (absolute); the maximum error was 2.2% (absolute). The relative % error in calculating the aromatic hydrocarbons varied from 0 to 13% (depending on the hydrocarbon content). The relative mean error was equal to 3.4%.

In order to test the repeatability, experiments, the results of which are not included in the present article, were carried out on the quantitative determination of aromatic hydrocarbons in 7 petroleum fractions. The mean deviation between duplicates amounted to 0.2% (absolute), the maximum deviation was 0.4%.

For a comparison of the proposed cryoscopic method for the determination of aromatic hydrocarbons with the aniline method [3], results are given for both methods in Table 5. The average value of the accuracy of the aniline method given in the table was derived from 7 experiments on synthetic mixtures; these results are not included for the sake of brevity. The relative accuracy of the aniline method (15%) was taken from the literature [4].

The values given in Table 5 show that, as regards accuracy and time spent and also the amount of sample necessary for an analysis, the cryoscopic method has considerable advantages over the aniline method. This is natural since the cryoscopic method is based on a physical law which is independent of the structure of the aromatic hydrocarbons or on the composition of the alkane-cyclane components. The aniline method is of an arbitrary nature and the results obtained when it is used depend on different factors, in particular on the composition of the alkanes and cyclanes composing the test fraction, and on the structure of the aromatic hydrocarbons.

It must be emphasized once again that when the cryoscopic method is used, the value found for the aromatic hydrocarbons content is expressed in mol %, as is usually done in the quantitative determination of unsaturated hydrocarbons by means of iodine and bromine numbers.

TABLE 3

Selection of the Optimum Conditions for H_2SO_4

Test No.	Composition of the Synthetic Mixtures		Conditions of treatment		Aromatic hydrocarbons in mix., %		Deviation Actual – Found	
	Cyclanes, alkanes	Aromatic hydrocarbons	Conc. of H_2SO_4, wt. %	Shaking duration, in min.	Actual	Found	Absolute %	Relative %
1	Cyclane-alkane part of the 200–250° fraction from Kalinsky petroleum.	1-Methylnaphthalene	99.1	60	29.9	29.1	+0.8	+2.7
2	Ditto	2-Phenylheptane	99.5	60	19.5	16.5	+3.0	+15.4
3	Ditto	Triethylbenzene	99.5	60	10.2	9.7	+0.5	+ 4.9
4	Ditto	Triethylbenzene + 1-Methylnaphthalene + 2-Phenylheptane	0.4 free SO_3	30	30.8	30.6	+0.2	+ 0.7
5	Cyclane-alkane part of the 250–300° fraction from Kalinsky petroleum.	Pentamethylbenzene	0.4 free SO_3	30	9.9	10.2	−0.3	− 0.3
6	Ditto	Pentamethylbenzene + Dibenzyl + Diamylnaphthalene	0.4 free SO_3	60	41.6	41.5	+0.1	+0.24
7	Cyclane-alkane part of the 300–350° fraction from Kalinsky petroleum.	Diamylnaphthalene	98.0	30	17.6	8.0	+9.6	+54.5
8	Ditto	"	0.1–0.2 free SO_3	30	17.6	17.5	+0.1	+ 0.6
9	Ditto	"	0.1–0.2 free SO_3	60	17.6	17.9	−0.3	− 1.7
10	Cyclane-alkane part of the 350–400° fraction from Buzovinsk petroleum.	Aromatic hydrocarbons from the 350–400° fraction of Buzovinsk petroleum	98.0	30	49.6	19.2	−30.4	−61.3
11	Ditto	Ditto	0.1–0.2 free SO_3	30	49.6	48.7	−0.9	− 1.8
12	Ditto	Ditto	0.1–0.2 free SO_3	60	51.8	50.8	+1.0	+ 1.9

TABLE 4

Checking the Cryoscopic Method for the Quantitative Determination of Aromatic Hydrocarbons on Synthetic Mixtures (amount of H_2SO_4 1 volume)

Test No.	Composition of Synthetic Mixtures		Conditions of H_2SO_4 treatment		Aromatic hydrocarbon content in mol.%		Deviation Actual-Found	
	Cyclanes and alkanes	Aromatic Hydrocarbons	H_2SO_4 conc., % wt.	Length of treatment in min.	Actual	Found	Absolute %	Relative %
1	2	3	4	5	6	7	8	9
1	Decahydronaphthalene	Diethylbenzene	99.1	60	9.4	9.0	+0.4	+5.0
2	Ditto	Ditto	99.1	60	10.2	9.7	+0.5	+5.0
3	"	"	99.1	60	9.9	10.0	-0.1	-1.0
4	"	"	99.1	60	10.0	10.0	0.0	0.0
5	Alkane-cyclane part from the 150-200° fraction of heavy Balakhany petroleum	Diethylbenzene	99.1	60	5.3	4.6	+0.7	+13.0
6	The same mixture	Ditto	99.1	60	5.3	4.6	+0.7	+13.0
7	Alkane-cyclane part of the 150-200° fraction of heavy Balakhany petroleum	"	99.1	60	11.3	10.0	+1.3	+19.0
8	The same mixture	Ditto	99.1	60	11.3	9.9	+1.4	+13.0
9	Alkane-cyclane part of the 150-200° fraction from Sibiel'batsky petroleum	"	99.1	60	10.2	10.7	-0.5	- 5.0
10	Ditto	Ditto	99.1	60	32.5	32.2	+0.3	+1.0
11	n-Hexadecane	Triethylbenzene	99.1	60	29.7	29.2	+0.5	+2.0
12	Alkane-cyclane part of the 200-250° fraction from Kalinsky petroleum	1-Methylnaphthalene	99.1	60	29.9	29.1	+0.8	+3.0
13	Ditto	Ditto	0.5% free SO_3	30	29.7	28.9	+0.8	+3.0
14	"	"	Ditto	60	30.0	29.4	+0.6	+2.0
15	"	Triethylbenzene (7.0%) 1-methylnaphthalene (16.9%) 2-phenylheptane (6.9%)	"	30	30.8	30.6	+0.2	+1.0
16	n-Hexadecane	1-Methylnaphthalene	"	30	18.4	18.1	+0.3	+2.0
17	Decahydronaphthalene	Ditto	"	60	19.4	20.3	-0.9	+5.0
18	Alkane-cyclane part of the 250-300° fraction of Kalinsky petroleum	Pentamethylbenzene	"	30	9.9	10.2	-0.3	-3.0

TABLE 4 (continued)

1	2	3	4	5	6	7	8	9
19	Alkane-cyclane part of the 250-300° fraction of Kalinsky petroleum	Diamylnaphthalene	0.5% free SO_3	60	15.2	14.8	+0.4	+3.0
20	Ditto	Pentamethylbenzene	"	60	9.9	10.2	-0.3	-3.0
21	"	Pentamethylbenzene (5.8%), 1,2-Diphenylethane (11.3%), Diamylnaphthalene (24.5%)	"	60	41.6	41.5	+0.1	+0.3
22	Alkane-cyclane part of the 300-350°fraction from Kalinsky petroleum	Diamylnaphthalene	0.1-0.2% free SO_3	30	17.6	17.5	+0.1	+0.6
23	Ditto	Ditto	Ditto	60	17.6	17.9	-0.3	-1.7
24	"	Dicyclohexylindane	"	30	11.5	11.1	+0.4	+3.4
25	"	Ditto	"	60	11.5	11.1	+0.4	+3.4
26	"	Diamylnaphthalene (10.8%), dicyclohexylindane (18%)	"	30	28.8	27.7	+1.1	+3.8
27	"	Ditto	"	30	28.8	28.0	+0.8	+2.8
28	"	"	"	60	28.8	28.1	+0.7	+2.4
29	"	Aromatic hydrocarbons 300-350° fraction from Buzovinsk petroleum	"	30	42.5	42.5	0.0	0.0
30	"	Ditto	"	30	42.5	41.7	+0.8	+1.9
31	"	"	"	30	6.4	6.7	-0.3	+4.7
32	"	"	"	30	6.4	6.5	-0.1	-1.6
33	Alkane-cyclane part of the 360-400°fraction from Buzovinsk petroleum	Aromatic hydrocarbons 350-400° fraction from Buzovinsk petroleum	"	30	49.6	50.5	-0.9	-1.8
34	Ditto	Ditto	"	30	49.6	48.7	+0.9	+1.8
35	"	"	"	30	26.2	28.2	-2.0	-7.6
36	"	"	"	30	26.2	26.9	-0.7	-2.7
37	"	"	"	30	51.8	49.6	+2.2	+4.3
38	"	"	"	60	51.8	50.8	+1.0	+1.9
39	"	"	"	30	7.0	6.9	+0.1	+1.4
40	"	"	"	30	8.6	8.2	+0.4	+4.7
		Mean deviation					0.6	3.4
		Maximum deviation.....					2.2	13.0

TABLE 3

Comparison of the Cryoscopic Method for the Quantitative Determination of Aromatic Hydrocarbons with the Aniline Method

Qualitative Index	Method	
	Cryoscopic	Aniline
Time taken for one analysis	3.5	8
Amount of test fraction necessary for one analysis in ml	0.3-0.5	20
Accuracy of the analysis:		
Absolute %	0.6	2.4
Relative %	3.4	15

SUMMARY

1. A new cryoscopic method has been developed for the quantitative determination of aromatic hydrocarbons in ligroin, kerosene and gas oil fractions of straight distillates.

2. The mean accuracy of the cryoscopic method is 0.6% (absolute) and 3.4% (relative). The average repeatability is 0.2% (absolute).

3. The quantitative determination of aromatic hydrocarbons in one fraction by the cryoscopic method takes 3½ hours, as against 8 hours by the aniline method. The amount of sample necessary for one analysis by the cryoscopic method is 0.3-0.5 ml as against 20 ml for the aniline method.

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A GENERAL METHOD FOR THE INVESTIGATION OF COPRECIPITATION AND ADSORPTION BY MEANS OF LABELLED ATOMS

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During the separation of elements prior to their analytical determination the undesirable phenomena of adsorption and coprecipitation often crop up. These phenomena interfere with the preperation of chemically pure precipitates and often lead to an increased weight of the latter with consequent analytical errors.

Adsorption and cocrystallization are of fundamental importance not only in analytical chemistry but also in a number of industries, e.g. in the separation of radioactive elements from their ores.

The most thorough and fundamental theories of adsorption and coprecipitation during the formation of precipitates were developed by Academician V.G.Khlopin and his school in a series of investigations begun in 1924 [1]. In recent years I.V.Tananaev has devoted a large number of investigations to the application of physico-chemical analysis to systems of analytical importance.

In one of these investigations [2] the solubility of nickel ferrocyanide in the presence of $K_4Fe(CN)_6$, $Na_4Fe(CN)_6$ and $Li_4Fe(CN)_6$ was studied, as well as the chemical composition of the precipitate.

The authors found that under certain conditions the nickel ferrocyanide precipitate during its formation could trap up to 10% of lithium ferrocyanide.

It is possible to determine the solubility of precipitates very simply by means of radioactive indicators using a new method proposed by us recently [3].

The phenomenon of coprecipitation during the formation of precipitates used in analytical practice can also be studied by means of radioactive isotopes.

Thus V.P.Shvedov in checking on the oxalate method of separating calcium from magnesium by means of radioactive calcium concluded that "it is possible to select conditions which lead to a decrease in the coprecipitation of calcium and magnesium, but to eliminate coprecipitation altogether is probably impossible" [4]. The same author in checking the sulfate method of separating calcium and magnesium by means of labelled atoms found that magnesium traps calcium while part of the latter remains in solution [5].

The use of radioactive lead as an indicator enabled V.P.Shvedov in another investigation to propose a method free from coprecipitation for the separation of lead as the oxychloride [6]. Undesirable coprecipitation also occurs in the gravimetric separation of anions.

Thus in the separation of the ortho and pyrophosphates of zinc and cadmium, Van-Straten and Aten using radiophosphorus found coprecipitation occurs to the extent of from 1 to 4% [7].

From the examples already cited it is clear how important adsorption and coprecipitation are for both theory and practical analysis. Insufficient investigation of this problem is undoubtedly connected with the difficulties of the

classical methods when applied to a large number of precipitates formed under various conditions of precipitation.

The use of labelled atoms which could facilitate the solution of these problems has not hitherto been systematically applied to the study of coprecipitation.

The present investigation was undertaken with the aim of developing a general method of studying adsorption and coprecipitation by means of radioactive isotopes. As the object for developing this technique we chose the widely used chromate method of separating barium from strontium.

Checking the Chromate Method

The chromate method for separating barium and strontium was proposed by Fresenius [8] and was subsequently introduced into the text books of analytical chemistry and into a number of All-Union standards.

Before precipitation a few drops of acetic acid are added to the neutral solution of barium and strontium salts and the precipitation in then accomplished by means of ammonium chromate, which according to Fresenius should be "more acid than alkaline". It is recommended that the precipitation be repeated under these conditions. The precipitate A obtained in this way is carefully calcined to constant weight. Strontium is precipitated from the filtrates as carbonate. The latter is dissolved and the strontium subsequently precipitated as the sulfate. This precipitate B is also calcined to constant weight.

Fresenius' method which was modified somewhat by Skrabal and Neustadt [9] was checked recently by Beyer and Rieman [10].

These last authors purely by calculation found that barium chromate should be precipitated at a pH of 4.6.

The precipitates which they obtained under these conditions had reliable weights. The weakness of their work lies in the absence of proof that these precipitates do not contain strontium.

In order to check on this point we carried out a large number of separations according to the Fresenius method, in which the volume of solution was approximately 100 ml in all cases. Results of one series of experiments are adduced in Table 1[1].

TABLE 1

Separation of Barium from Strontium. Results of Gravimetric Determination

No. of expt.	Ba Calc. as $BaCrO_4$			Sr Calc. as $SrSO_4$		
	Taken, in mg	Found		Taken, in mg	Found	
		mg	Percent		mg	Percent
7	62.5	62.8	100.5	46.6	45.8	98.3
8	62.5	64.8	103.5	46.6	44.8	96.0
9	62.5	66.2	106.0	46.6	43.8	94.0
10	62.5	65.8	105.4	46.6	44.0	94.5
11	111.6	137.2	123.5	–	–	–
12	111.6	112.0	100.5	121.0	119.3	98.8

As the results in Table 1 show, gravimetric determination in a number of cases gave completely satisfactory results. In others however even for the determination of barium, inadmissible errors of 3-6% were obtained.

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[1] V.V.Bogacheva carried out a large number of experiments on the precipitation and determination of the activity of the precipitates obtained.

In some cases, as e.g. in experiment 11, the error in the determination of barium exceeded 23%.

In order to explain these deviations, we decided to carry out a number of tests on the separation of barium from strontium by the chromate method using the radioactive isotope Sr^{89}; its characteristics viz a half life of $T_{50\%}$ = 55 days and comparatively hard β-rays make it suitable for this purpose.

Having prepared standards containing a known amount of strontium and comparing its activity with the activity of the precipitates, we could easily determine the actual amount of strontium in the $BaCrO_4$ and $SrSO_4$.

Some results of such determinations are given in Table 2.

In Column 3, Table 2, results are given for the gravimetric determination of $BaCrO_4$ which agree fairly well with the amount of barium actually taken. On the other hand radiometric determinations show that the $BaCrO_4$ contains about 7% $SrCrO_4$. This means, that part of the barium is still in solution and is subsequently precipitated as sulfate together with the strontium.

TABLE 2

Separation of Barium from Strontium. Results of Gravimetric and Radiometric Determinations.

No. of expt.	Amount of barium taken calcd. as $BaCrO_4$, mg	Found in mg			Amount of strontium taken calcd as $SrSO_4$, mg	Found in mg		
		$BaCrO_4$+ +$SrCrO_4$	$BaCrO_4$	$SrCrO_4$		$SrSO_4$+ +$BaSO_4$	$SrSO_4$	$BaSO_4$
13	62.5	63.8	59.6	4.2	51.6	50.1	47.0	3.1
14	62.5	61.4	57.5	3.9	51.6	51.1	45.7	5.4
15	62.5	63.8	59.9	3.9	51.6	48.3	45.5	2.8
18	62.5	61.4	57.3	4.1	51.6	50.8	45.5	5.6
19	62.5	61.8	57.7	4.1	51.6	50.8	45.6	5.2
20	62.5	62.2	57.7	4.5	51.6	45.8	40.7	5.1

Similar conclusions were reached after determining the specific activity of the $SrSO_4$; the activity was depressed by 6-11%, indicating that a considerable amount of barium accompanies the strontium in the sulfate precipitate. All these relations are shown clearly by consideration of Columns 8 and 9 in Table 2. These experiments showed that the comparatively good results obtained for the determination of barium in the presence of strontium by the Fresenius' method is explained not so much by the merits of the method but by the fortuitous compensation of two errors.

It is obvious that for small variations in the precipitation conditions one should expect a considerable change in the amount of strontium trapped by barium and that this should lead to marked deviations in the analytical results, similar to that deviation which we observed during consideration of Table 1.

It should be interesting to explain whether or not the trapping of stontium is the result of adsorption on the barium chromate precipitate or of coprecipitation. In order to do this we carried out a number of experiments which are described below.

Investigation of the Adsorption of Strontium on $BaCrO_4$

In the experiments on the study of adsorption we precipitated $BaCrO_4$ separately as described above and only afterwards was the solution of $Sr^{89}Cl_2$ poured into the beaker containing the precipitate. The solution and precipitate were mixed

several times in the course of 1 hour, after which the precipitate of $BaCrO_4$ was filtered off, washed, and then calcined to constant weight. The activity of the precipitate was measured with a counter. Results of experiments carried out at different pH values are given in Table 3.

The results in Table 3 show that adsorption of strontium on $BaCrO_4$ in acid, neutral or weak basic solutions does not exceed 1.2%. Only at a pH ≥ 9.5 is a sharp increase in activity of the precipitate observed. This is undoubtedly connected with the formation and adsorption of hydrated oxides of strontium of a white color. The relation between adsorption and pH is depicted in Fig. 1 (Curve 6).

TABLE 3

Adsorption of Sr on $BaCrO_4$ precipitates in a solution containing $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$. Activity of the standard I_0 = 2800 impulses/minute

No. of expt.	pH of solution	Activity of ppt., impulses/minute	$\frac{100\ I}{I_0}$
23	6.5	28	1.0
24	8.0	34	1.2
25	8.3	32	1.1
26	9.0	28	1.0
27	9.2	30	1.1
28	9.5	910	32.5
29	9.8	1532	54.7

It is known that in some instances precipitates can be formed during a change in pH as a result of the suppression of the dissocation of the precipitant, in our case chromic acid. However simple calculations on the basis of the soubility product of $BaCrO_4$ ($K_1 = 2.10^{-10}$) [11] and $SrCrO_4$ ($K_2 = 4.10^{-5}$) [12] and also of the first dissociation constant of H_2CrO_4 ($K = 7.10^{-3}$) [13] show that under the conditions of our experiments the precipitation of $SrCrO_4$ cannot occur in the absence of $BaCrO_4$.

These calculations together with the experiments described above show that the significant trapping of strontium during the formation of $BaCrO_4$ precipitates is explained not so much by adsorption and independent precipitation of strontium, as by its coprecipitation.

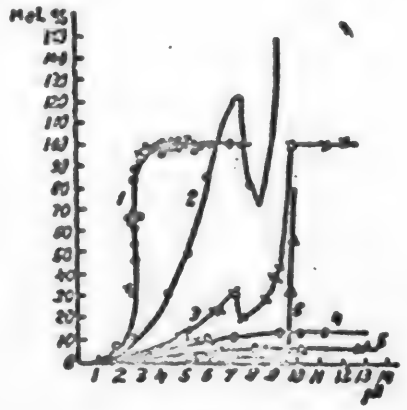

Fig.1. Adsorption and coprecipitation of barium and strontium chromates: 1-precipitation of $BaCrO_4$ from a mixture of $2.46 \cdot 10$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$ for different pH values. (Circles denote results obtained by measurement of the activity of Ba^{140}, while crosses denote results obtained gravimetrically). Curves for coprecipitation of $SrCrO_4$ with $BaCrO_4$ from solutions containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and different amounts of $SrCl_2$. Curve 2-$12.3 \cdot 10^{-4}$ mol/l; Curve 3-$2.51 \cdot 10^{-4}$ mol/l; Curve 4-$0.5 \cdot 10^{-4}$ mol/l and Curve 5-$0.25 \cdot 10^{-4}$ mol/l; Curve 6-adsorption of Sr on $BaCrO_4$. All results are expressed in mol. percent in relation to the amount of $BaCl_2$ taken.

Investigation of the Coprecipitation of $SrCrO_4$ with $BaCrO_4$

The coprecipitation of strontium and barium was studied in a wide pH range, using the radioisotopes Ba^{140} and Sr^{89} as controls.

The original solution of $BaCl_2$ had a concentration of $2.46 \cdot 10^{-4}$ mol/l. The concentration of $SrCl_2$ in the same solution amounted to $2.51 \cdot 10^{-4}$ mol/l. Precipitation was accomplished either by the Fresenius method as described above or as follows.

To the test solution about 2 ml of 36% HCl is added, followed by an excess of ammonium chromate. When these conditions are observed the hydrogen ion concentration is so high that the barium chromate is not precipitated. Next dilute ammonia (2.5%) was added dropwise to the solution until the requisite pH was obtained. The pH was measured after precipitation of the chromates by means of a pH-meter incorporating a glass electrode.

Comparison of both methods showed that the order of precipitation which we proposed leads to a considerable decrease in the amount of strontium trapped by barium chromate. As a result all the experiments carried out henceforth were made by addition of hydrochloric acid with subsequent neutralization with ammonia instead of Fresenius' method.

In the first series of experiments we used the Ba^{140} isotope and inactive strontium. Having prepared the radiobarium standard and measured the activity of the precipitate at different pH values, we got the results adduced in Table 4.

The results in Table 4 show that precipitates of $BaCrO_4$ on addition of ammonia begin to be formed when the pH $\geq$1. On increasing the pH the percentage of barium precipitated gradually increases and at pH=4.5 complete precipitation of barium is observed.

In all the experiments on coprecipitation, the concentration of $BaCl_2$ was $2.46 \cdot 10^{-4}$ mol/l. All the experiments described below were carried out with Sr^{89}.

TABLE 4

Precipitation of $BaCrO_4$ from solutions containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$. The activity of the standard was I_0=760 impulses/minute.

No. of expt.	pH of solution	Activity of ppt. I, imp./min.	$\frac{100\,I}{I_0}$	No. of expt.	pH of solution	Activity ppt. I, imp/min.	$\frac{100\,I}{I_0}$
30	1.8	57	7.5	46	3.6	746	98.1
31	2.1	20	2.6	47	3.8	756	99.6
38	2.1	18	2.4	48	4.0	726	95.5
32	2.5	240	31.7	49	4.2	745	98.0
39	2.3	480	63.6	57	4.2	764	100.0
43	2.5	500	66.0	50	4.4	758	100.0
33	2.6	465	61.0	58	4.4	738	97.0
40	2.7	351	46.2	52	4.7	762	100.0
41	2.7	514	67.5	53	5.0	760	100.0
44	2.7	630	83.0	54	5.5	741	97.5
34	2.8	669	88.0	59	5.5	760	100.0
42	3.0	697	91.8	55	5.7	752	99.0
45	3.0	510	67.1	56	6.2	759	100.0
35	3.3	745	97.8	60	7.1	763	100.0
36	3.4	744	97.8	61	7.7	762	100.0

In the first series of experiments a concentration of $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$ was employed.

The results of the first series of experiments which was conducted within a wide pH range are given in Table 5.

From a consideration of Table 5 and curve 3, Fig. 1, it can be seen that the first sign of coprecipitation of strontium is observed at pH > 1.5. It is interesting to note that coprecipitation increases up to pH 7.2. On increasing the pH further, coprecipitation at first decreases and then increases again. Minimum coprecipitation occurs at pH ≈7.5.

TABLE 5

Coprecipitation of $SrCrO_4$ with $BaCrO_4$, in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$.
I_o = 1430 impulses/min.

Expt. No.	pH solution	Activity of ppt. I, imp./min.	$\frac{100\ I}{I_o}$
62	1.8	14	1.0
63	2.3	26	1.8
64	2.7	50	3.5
65	4.2	100	7.0
66	4.9	160	11.2
67	5.0	199	14.0
68	6.3	336	23.5
69	6.5	343	24.0
70	7.3	443	31.0
71	7.6	300	21.0
72	8.5	393	27.5
73	8.9	565	39.5
74	9.1	572	40.0
77	9.2	622	43.5
78	9.9	1432	100
79	11.4	1416	99
80	12.4	1431	100

The second series of experiments was carried out with a solution containing $0.5 \cdot 10^{-4}$ mol/l $SrCl_2$. Results on the determination of the activity of strontium, which increases with formation of $BaCrO_4$ precipitates, are given in the third column of Table 6.

In Column 4, Table 6, the relative amounts of $SrCrO_4$ trapped by $BaCrO_4$ are compared. They are expressed in molar percentages in relation to the amount of $BaCl_2$ taken.

The results of our determinations are depicted in Fig.1, Curve 4.

The third series of experiments was carried out on a solution of $SrCl_2$, the concentration of which was $0.25 \cdot 10^{-4}$ mol/l. Results are given in Table 7 and in Fig. 1 (Curve 5).

In the case just described, as in previous series of experiments, we did not observe a sharp increase in coprecipitation in alkaline solutions. This is explained apparently by the low concentrations of $SrCl_2$, which cannot ensure the formation of a precipitate of hydrated strontium oxide.

The fourth series of experiments was carried out with $SrCl_2$ solution the concentration of which was $12.3 \cdot 10^{-4}$ mol/l, i.e., a molar ratio of Sr:Ba = 5:1.

The results of the experiments carried out with solutions of this concentration are adduced in Table 8 and in Fig. 1 (Curve 2).

In the case of the comparatively concentrated $SrCl_2$ solution the maximum coprecipitation which is observed at pH 7.5 is particularly clearly defined. Consideration of Fig.1, in which results are given for the coprecipitation of strontium with barium chromate for various relative concentrations and at different pH values, enables one to understand why the Fresenius' method gives widely different results for small, practically imperceptible changes in the precipitation conditions.

Precipitation of Barium Chromate at Different pH Values

In order to check the results we carried out a few series of experiments on the separation of barium and strontium by the chromate method. The concentration of the $BaCl_2$ and $SrCl_2$ were $2.46 \cdot 10^{-4}$ mol/l and $2.5 \cdot 10^{-4}$ mol/l respectively. The pH of the solution was determined both before and after formation of the precipitate by means of a pH-meter and glass electrode.

TABLE 6

Coprecipitation of $SrCrO_4$ with $BaCrO_4$ in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $0.5 \cdot 10^{-4}$ mol/l $SrCl_2$. I_o = 1620 impulses/min

Expt. No.	pH of solution	Activity of ppt. I, imp/min.	$\frac{100\ I}{5\ I_o}$
81	4.7	406	5.0
82	5.1	403	5.0
83	6.0	721	8.9
84	6.1	648	8.0
85	7.3	906	11.2
86	9.3	1002	13.6
88	10.2	1134	14.0
89	11.3	1100	13.6

TABLE 7

Coprecipitation of $SrCrO_4$ with $BaCrO_4$ in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $0.25 \cdot 10^{-4}$ mol/l $SrCl_2$. I_o = 1510 impulses/min

Expt. No.	pH of solution	Activity of ppt. I, imp/min.	$\frac{100\ I}{10\ I_o}$
90	5.1	445	3.0
92	6.0	785	5.2
93	6.4	830	5.5
94	6.6	756	5.0
95	7.1	724	4.8
97	7.6	620	4.1
98	8.5	718	4.6
99	9.5	831	5.5
100	10.6	829	5.5
101	12.5	846	5.6

The precipitate of $BaCrO_4$ containing various amounts of $SrCrO_4$ was filtered, washed and carefully calcined to constant weight (Precipitate A). The filtrate was evaporated and the strontium carbonate (contaminated with barium) precipitate formed thereby filtered off, washed, and dissolved in hydrochloric acid.

TABLE 8

Coprecipitation of $SrCrO_4$ with $BaCrO_4$ in a solution containing $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $12.3 \cdot 10^{-4}$ mol/l $SrCl_2$. I_o = 1560 impulses/min

Expt. No.	pH of solution	Activity of ppt. I, imp./min.	$\frac{100\ I}{0.2\ I_o}$
104	4.2	94	30.0
105	5.0	156	50.0
106	5.4	226	72.5
107	7.7	380	75.0
108	8.0	265	85.0
109	8.3	234	75.0
110	9.2	468	150.0
112	9.9	1015	325.0

Ethyl alcohol was then added and the mixture of sulfates precipitated from the solution. The gravimetric determination of these sulfates was carried out by the usual method (Precipitate B).

Using the results adduced in Tables 4-8 and in Fig.1, it is easy to calculate the composition of precipitates A and B.

Results of such calculations and also the results of the gravimetric determinations are compared in Table 9.

The calculated curves expressing the relations between the precipitates A and B and the pH are depicted in Fig. 2. These curves show that the experimental points lie close to the calculated curves.

From a consideration of Fig. 2 it follows that on precipitation from acid solution precipitate A has a small weight, but on precipitation from neutral and alkaline solutions its weight is too much. The weight of precipitate B changes in the reverse direction. Therefore a value of the pH always exists at which a weight of precipitate A can be obtained which corresponds to a complete separation of barium. Of course this precipitate with a "theoretical" weight is really a mixture of $BaCrO_4$ and $SrCrO_4$.

It is obvious that in working out the chromate method for the separation of

TABLE 9

Amounts of $BaCrO_4$ and $SrCrO_4$ Precipitates Calculated from the Precipitation Curves and Found Gravimetrically

Expt. No.	pH	Calculated $BaCrO_4$ + $SrCrO_4$, in mg	Weight of ppt. A, in mg	Calculated $SrSO_4$ + $BaSO_4$, in mg	Weight of ppt. B, in mg
115	1.6	1.0	4.5	103.0	99.8
116	2.0	1.6	1.0	102.0	100
117	2.2	2.0	2.3	101.5	99.6
118	2.5	20.0	20.5	90.0	91.7
119	2.6	38.0	38.0	78.0	-
141	2.6	38.0	41.0	78.0	67.0
152	2.6	38.0	42.8	78.0	63.9
120	2.7	52.0	31.6	57.0	75.0
142	2.7	52.0	34.5	57.0	63.2
121	2.7	53.0	52.8	57.0	56.6
143	2.8	56.5	56.5	51.0	50.8
122	3.0	58.7	58.5	48.0	48.5
144	3.2	60.0	60.8	47.0	47.0
123	3.3	60.5	61.2	46.5	-
124	3.6	61.8	61.0	45.8	46.2
125	3.8	62.9	64.0	45.0	44.7
126	4.0	63.5	63.4	44.5	44.5
145	4.1	63.8	63.3	44.0	-
127	4.2	64.0	64.0	43.8	-
146	4.2	64.0	65.9	43.8	42.0
129	4.4	65.0	64.7	43.0	43.4
147	4.4	65.0	65.4	43.0	44.8
130	4.5	65.4	65.4	42.6	42.1
131	4.7	66.0	64.5	41.8	63.2
132	4.8	66.5	66.5	41.5	42.8
133	5.0	67.3	69.0	41.0	40.9
148	5.1	67.8	66.0	40.5	41.7
134	5.2	68.2	67.0	40.0	41.5
135	5.5	69.2	70.0	39.0	38.0
149	5.5	69.2	68.3	39.0	40.3
150	5.5	69.2	71.0	39.0	37.7
136	5.5	69.2	67.7	39.0	40.0
137	6.0	71.0	71.2	37.5	37.6
138	6.4	73.5	73.2	35.0	35.2
139	6.9	76.0	73.5	33.0	36.0
140	7.6	79.0	81.0	30.5	28.4

barium from strontium, as for a number of other similar analytical methods, the efforts of investigators were directed to creating such conditions for precipitation as would ensure obtaining a precipitate of the expected weight. Under these conditions, the precipitate is determined not by the exact pH value of the solution but by more or less approximate procedures for the preparation of the latter.

The chemical perception of good researchers is exemplified by the fact that at the point corresponding to the expected weight of $BaCrO_4$ precipitate (see Fig.2) the solution appears actually to be in accordance with Fresenius' observation "more acid than alkali".

Maximum Coprecipitation

The results which we obtained on the coprecipitation of strontium chromate with barium chromate are characterized by a maximum within a definite pH range.

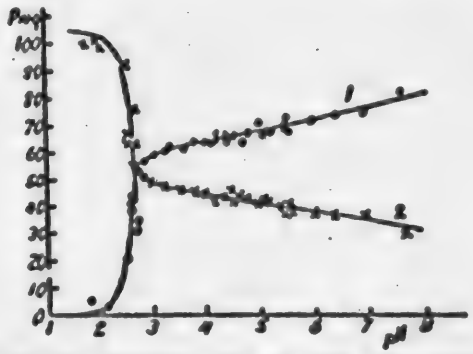

Fig.2. Relation between the pH and the weight of the chromate precipitates A (curve 1) and sulfates B (curve 2) during the separation of barium from strontium.

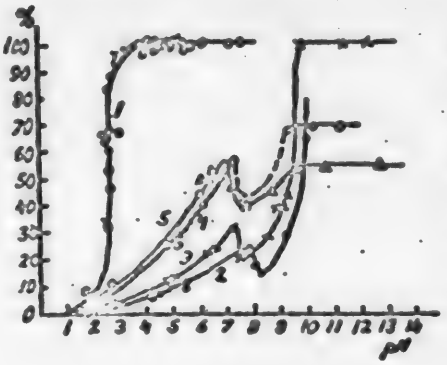

Fig.3. Coprecipitation of $SrCrO_4$ with $BaCrO_4$. All the original solutions contain $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and different amounts of $SrCl_2$: $12.3 \cdot 10^{-4}$ mol/l (curve 2); $2.51 \cdot 10^{-4}$ mol/l (curve 3); $0.5 \cdot 10^{-4}$ mol/l (curve 4) and $0.25 \cdot 10^{-4}$ mol/l (curve 5); Curve 1 shows the precipitation of $BaCrO_4$ for different pH values and curves 2-5 the percentages of $SrCrO_4$ coprecipitated.

This maximum is particularly clearly shown on the coprecipitation pH curve, when the amount of trapped strontium is expressed as a percentage of the amount taken.

Curves of this type are depicted in Fig.3. The pH corresponding to maximum coprecipitation in all cases lies in the 7.2–7.8 range and on an average is equal to 7.5.

The fact that maximum coprecipitation does occur as we have shown can be explained on the assumption that the growth of $BaCrO_4$ crystals proceeds as a result of the transfer of Ba^{++} and CrO_4^{--} ions from solution. Cocrystallization of strontium may proceed only through the stage of adsorption of Sr^{++} ions.

Under these conditions the velocity of strontium coprecipitation is proportional to its adsorption. The latter value according to the Langmuir isotherm is expressed as follows:

$$\theta_{Sr} = \frac{a_{Sr^{++}}[Sr^{++}]}{1 + a_{Sr^{++}}[Sr^{++}] + a_{H^+}[H^+] + a_{OH^-}[OH^-]} \qquad (1)$$

Here θ_{Sr} is the part of the surface of a growing crystal occupied by adsorbed strontium ions; $a_{Sr^{++}}$, a_{H^+} and a_{OH^-} are the adsorption coefficients for strontium, hydrogen, and hydroxyl ions respectively.

It is clear that the velocity of coprecipitation

$$W = k\,\theta_{Sr} = \frac{k a_{Sr^{++}}[Sr^{++}]}{1 + a_{Sr^{++}}[Sr^{++}] + a_{H^+}[H^+] + a_{OH^-}[OH^-]} \qquad (2)$$

As is known,

$$[OH^-] = \frac{10^{-14}}{[H^+]}. \qquad (3)$$

Then substituting for $[OH^-]$ in (2) we get:

$$W = \frac{k a_{Sr^{++}}[Sr^{++}]}{1 + a_{Sr^{++}}[Sr^{++}] + a_{H^+}[H^+] + a_{OH^-}\frac{10^{-14}}{[H^+]}} \qquad (4)$$

In order to find the maximum coprecipitation of Sr in relation to hydrogen ion concentration we equate $dW/d[H^+]$ to zero. The following equation is then obtained:

$$a_{H^+} - \frac{10^{-14} \cdot a_{OH^-}}{[H^+]^2} = 0. \qquad (5)$$

It is obvious that maximum coprecipitation of strontium corresponds to the hydrogen ion concentration

$$[H^+] = 10^{-7}\sqrt{\frac{a_{OH^-}}{a_{H^+}}}. \qquad (6)$$

This concentration corresponds to the value of the pH indicator.

$$pH = 7 + \frac{1}{2}\log\frac{a_{H^+}}{a_{OH^-}}. \qquad (7)$$

According to our experiments, maximum coprecipitation is observed at a pH of approximately 7.5. Substituting the value of the pH in formula (7) we find that

$$\frac{1}{2}\log\frac{a_{H^+}}{a_{OH^-}} \approx 0.5. \qquad (8)$$

This means that if our hypothesis re the mechanism of the crystallization of $SrCrO_4$ is correct then

$$\frac{a_{H^+}}{a_{OH^-}} \approx 10, \qquad (9)$$

i.e., the hydrogen ions are adsorbed practically 10 times better than the hydroxyl ions on the surface of the $BaCrO_4$ crystals.

If the mechanism which we have proposed for coprecipitation is correct the amount of the latter should depend strictly on the concentration of surface active materials in solution.

In this connection we carried out a number of tests in which various amounts of gelatin were added to the solution.

Coprecipitation of Strontium in the Presence of Gelatin

Experiments in which gelatin was added in amounts ranging from 0.001 to 0.03% were carried out with a solution containing $2.51 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$. Precipitation was carried out either by the Fresenius' method or our method. These experiments showed that when our method is adopted the amount of strontium coprecipitated decreases by 1.5-2 times. All the experiments described below on the precipitation of $BaCrO_4$ in the presence of gelatin were therefore carried out by the addition of hydrochloric acid followed by a gradual neutralization with ammonia.

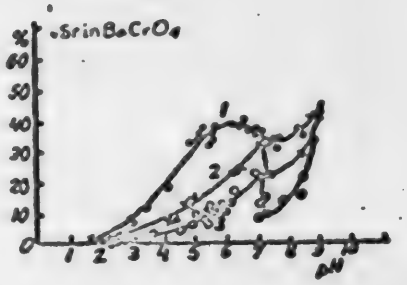

Fig.4, Trapping of strontium during precipitation of $BaCrO_4$ by Fresenius' method (Curve 1), by our method (Curve 2) and by our method in the presence of 0.01% gelatin (Curve 3). In all the experiments the solutions contained $2.46 \cdot 10^{-4}$ mol/l $BaCl_2$ and $2.51 \cdot 10^{-4}$ mol/l $SrCl_2$.

Our experiments showed that on increasing the concentration of gelatin from 0.001 to 0.01% the amount of strontium coprecipitated gradually decreased. Further increases in the amount of gelatin from 0.01 to 0.03% did not have any effect on the amount of strontium precipitated. It is highly probable that 0.01% gelatin is sufficient for filling up the surface of the growing crystals of $BaCrO_4$. In this connection therefore it is possible to recommend that precipitation of $BaCrO_4$ should be carried out from solutions containing strontium in the presence of 0.01% gelatin.

We carried out comparative experiments of this type on the study of the trapping of strontium during the precipitation of $BaCrO_4$ by Fresenius' method and by our method with and without gelatin.

The results obtained are given in Fig. 4. These curves show that Fresenius' method leads to a considerably higher trapping of strontium than our method does. Coprecipitation is even less when our method is used in conjuction with the use of 0.01% gelatin.

The results which we obtained on the relation between coprecipitation and the concentration of the components of the solution, and other parameters enable the problem of coprecipitation to be considered from the general point of view of physico-chemical analysis.

Physico-Chemical Diagram of Coprecipitation

Physico-chemical analysis was first used by I.V.Tananaev for investigating systems of importance in analytical chemistry. In particular he studied in detail the effect of certain sulfates and nitrates on the solubility of $PbSO_4$. The results enabled him to construct a number of physico-chemical diagrams characterizing the precipitation of lead sulfate under different conditions [14,15,16].

It seems to us that a physicl-chemical diagram on the ordinate of which is plotted a new property "coprecipitation", should play an important part in analytical chemistry. The construction of such diagrams by the classical methods is a

very difficult problem. The method of radioactive indicators as we have shown in the present article allows this problem to be solved fairly easily. Such a method has not hitherto been described in the literature [17].

Two dimensional physico-chemical diagrams of "coprecipitation pH" were given in Figs. 1 and 2. The results which we obtained for coprecipitation at different relative concentrations of Sr/Ba and at different pH values allows a three dimensional physico-chemical diagram of coprecipitation of the type shown schematically in Fig. 5 to be drawn.

The amount of coprecipitation expressed as a percentage of the amount of barium taken is plotted along the vertical axis A while the pH values and the value of Sr/Ba are plotted on the horizontal axis of the three dimensional diagram, respectively

The amount of coprecipitation is characterized by a complex surface with a crest and a hollow corresponding to maximum and minimum values of the amount of strontium in the precipitate. The spatial disposition of this surface relief is also shown by a consideration of Figs. 5 and 6.

By means of the coprecipitation diagram it is possible to choose rationally conditions for subsequent precipitation of $BaCrO_4$ such as will ensure obtaining a precipitate of the requisite purity with a minimum waste of time and labor. To achieve this end it is necessary to carry out subsequent precipitations under those conditions where the line of the process corresponds to a minimum coprecipitation of strontium for complete precipitation of barium. As shown in Fig. 1, this condition is observed at a pH of 5. The value of the pH should be controlled by means of a pH meter.

If precipitation is carried out by Fresenius' method in equimolar solutions at a pH of 5, about 30% of strontium is trapped.

The order of precipitation proposed by us (addition of hydrochloric acid and gradual neutralization with ammonia) decreases the amount of strontium trapped to 12%.

Finally our method in conjuction with the use of 0.01% gelatin lowers the amount of strontium coprecipitated to 6%.

It is possible by using a physico-chemical diagram of coprecipitation to start with a solution containing equivalent amounts of barium and strontium and, by precipitating twice, separate barium containing less than 1% strontium completely, and get complete agreement with theory.

To get such a result by means of the old empirical method would necessitate not less than 4 reprecipitations.

The method of investigating coprecipitation with the aid of radioactive isotopes is of a general character and can be applied for investigating a large number of different systems which are important in analytical chemistry.

SUMMARY

1. A general method has been worked out for investigating coprecipitation by means of radioactive indicators.

2. The relation of coprecipitation of $SrCrO_4$ and $BaCrO_4$ to their relative concentrations and at different pH values has been studied.

3. Maximum coprecipitation was found to occur at a definite pH.

4. A new property is introduced into physico-chemical analysis, "coprecipitation", and a three dimensional diagram is constructed for the coprecipitation of strontium chromate and barium chromate.

5. By means of the three-dimensional physico-chemical diagram of coprecipitation, improvements are introduced into the chromate method for the separation of barium from strontium.

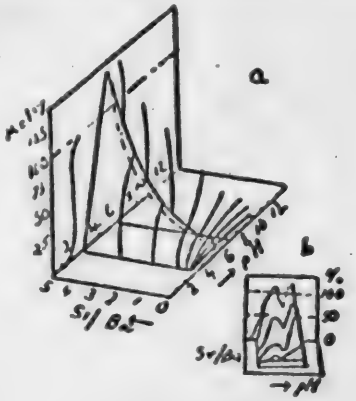

Fig. 5. Three-dimensional diagram of coprecipitation of Sr and $BaCrO_3$ at different values of Sr/Ba and pH.

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A COLOR REACTION FOR FLUORIDE IONS USING TITANIUM-CHROMOTROPIC ACID REAGENT

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It is well known that the fluoride ion does not form colored compounds. In order to determine fluorides colorimetrically therefore their property of decolorizing colored compounds of certain metals is used. The complexes of zirconium or thorium with alizarin, ferric thiocyanate and the compound of titanium with hydrogen peroxide are most often used as the colored complexes. The determination of fluorides by means of zirconium and thorium complexes and also of iron cannot be carried out in the presence of sulfates and phosphates, since these anions give rise to practically the same decolorizing effect as the fluoride ion.

This drawback of course is connected with the use of zirconium, thorium, and iron and cannot be eliminated by the substitution of the alizarin or thiocyanate complexes with some other colored compounds of these metals.

The drawback of the peroxide compound of titanium as a reagent for fluorides is the low sensitivity of the reaction which is determined by the weak color of the titanium peroxide. The sulfate ions do not interfere appreciably because they do not form stable complexes with titanium. Phosphates in small amounts also do not interfere with the determination. In order to detect fluoride ions, therefore, it is expedient to use colored complex compounds of titanium, which, however, have a higher molar concentration of absorption than titanium peroxide complexes.

The Sensitivity of Reactions for the Fluoride Ion Using Certain Colored Complexes of Titanium

The most characteristic expression of the sensitivity of a color reaction is the molar coefficient of absorption of colored compounds. Results are given in the diagram of absorption curves for certain colored complexes of titanium with a series of reagents such as hydrogen peroxide (Curve 1); alizarin (2); pyrocatechol (3), tannin (4), chromotropic acid (5). The curves were obtained by measuring the absorption by means of an FM photometer fitted with various light filters. The solutions were prepared as follows: in all cases a ten-fold excess of reagent of reagent with respect to titanium was used. This ensures that the titanium is all combined as the complex. The concentrations of the colored solutions with respect to titanium was always 0.0002 M with the exception of the peroxide compounds. In the case of the peroxides 0.1 M solution with respect to titanium was used. The pH of the solution was 1 (for the peroxides) and 3 for the remainder. The results adduced in the diagrams show that of the groups studied the most sensitive reagent for titanium is chromotropic acid. The molar coefficient of absorption of the titanium-chromotropic acid complex was roughly 100 times that of the peroxide compound of titanium.

The colored compound of the metal can be used as a reagent for the fluoride ion only when the fluoride complex of the metal under certain conditions is more stable than the colored complex of this metal.

In order to solve this question for the titanium complexes indicated above, the following experiments were carried out. The minimum amount of sodium fluoride necessary for half decolorizing the given complex was determined, the concentration of complexes being selected so that the intensity of their colors was approximately equal. Each solution was divided up into two lots of 10 ml each. One lot was diluted by the addition of an equal volume of water, while the other lot was titrated with 0.02 M sodium fluoride solution from a microburet until the colors of the first and second lots were the same. The results are given in the Table.

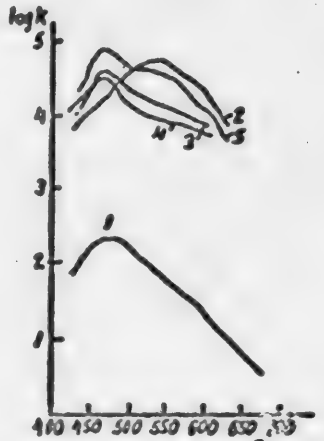
It was found that the titanium-chromotropic acid reagent needed the smallest amount of sodium fluoride. Thus, the most suitable reagent for the fluoride ion is this complex of titanium and chromotropic acid, which satisfies the above conditions.

Effect of pH on the Color Intensity of the Titanium-Chromotropic Acid Complex

In order that solutions of titanium salts should not hydrolyze they should contain excess mineral acid. The pH of the solution, however, affects the color intensity of the titanium-chromotropic acid complex. In strong acid media a compound is formed which is colored bright red, the intensity of the color increasing on increase of the pH until a maximum is reached at a pH of 3. On increasing the pH further (pH 5), the solution changes color. The red complex acquires a yellow color, which is not decolorized on the addition of fluorides. A pH of 3 is therefore the optimum. The necessary hydrogen ion concentration is attained by use of a buffer of monochloracetic acid and its salts. In the following experiments we used a 0.1 N solution of monochloroacetic acid, half neutralized with 0.1 N alkali. The pH of this mixture is 2.85.

Increasing the Sensitivity of the Reaction and Preparation of the Reagent for the Color Reaction

In the presence of fluoride ions the red color of the titanium-chromotropic acid complex weakens as a result of the formation of the complex ion $[TiF]^{3+}$ or $[TiOF]^{+}$. The free chromotropic acid which separates out during this reaction is practically colorless. Thus, the presence of fluorides leads to a weakening of the color. It is accepted that the eye is far more sensitive to change in color that to a weakening of the color. The change in color will be more evident if a blue dye which is stable in acid media such as methylene blue is added to the solution of the titanium-



Reagent	Conc. of titanium, in mol.	Conc. of reagent, in mol.	Amount of 0.02 mol NaF, necessary for decolorization of solution by 50%, in ml.
Chromotropic acid	10^{-3}	10^{-3}	0.2
Tannin	10^{-3}	1%	0.3
Pyrocatechol	10^{-3}	10^{-3}	0.4
Alizarin	10^{-3}	10^{-3}	0.6
Hydrogen peroxide	$2{,}5 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	0.8

chromotropic acid complex. The mixture of this dye with the red titanium-chromotropic acid complex has a brown color. On addition of fluoride ions a fairly sharp change in the color of the solution from brown to blue can be observed. This enables very small changes in the color of the solution to be observed and increases the sensitivity of the reaction.

PROCEDURE

Reagent.

1) Solution of titanium sulfate; 1.6 g of the basic titanium sulfate $TiOSO_4$ is dissolved in 50 ml sulfuric acid (1:1) with heating. The solution is diluted with water and the titanium hydroxide precipitated with ammonia. This precipitate is filtered, washed, and dissolved in 50 ml of 1.5 mol/l sulfuric acid. The volume of solution is made up to 100 ml with the same acid solution. An approximately 0.1 M solution of titanium sulfate is thus obtained. The exact strength is determined gravimetrically. This solution serves as the base solution for making up less concentrated solutions.

2) A solution of chromotropic acid (1,8-dihydroxynaphthalenesulfonic acid) is prepared by dissolving 0.4 g of the dry compound in 1 liter of water. On standing the solution darkens; it is better therefore to use freshly prepared reagent.

3) A 0.01% solution of methylene blue in water.

4) Buffer solution. 0.945 g of monochloracetic acid is dissolved in 100 ml of water (0.1 mol/l solution). 25 ml of this solution is titrated with 0.1 N NaOH using phenolphthalein. To the remaining solution of monochloracetic acid 0.1 N alkali is added so that the solution is half neutralized. The pH of the final

solution is equal to pK for monochloroacetic acid (2.85).

For the determination of fluorides in solution a reagent is prepared which includes the following components; 5 ml of a 10^{-2} mol/liter solution of titanium sulfate, 1 ml of a 10^{-3} mol/liter solution of chromotropic acid, 1 ml of the methylene blue solution, and 1 ml of the buffer. The reagent can be stored for several months in a dark place.

1 ml of the reagent is added to 1-2 ml of the test solution. The presence of 4 µg of fluoride ions in this volume gives rise to an immediate change in color. For lower concentrations of fluoride the color change only occurs after some time. Thus, if the fluoride content is 0.- µg, the color changes after 10-15 minutes. If the reagent is used without a dye (methylene blue), the minimum amount of fluoride necessary to cause an observable change in color amounts to 4 µg in 2 ml. Lower concentrations even after long standing cause no appreciable decolorization of the reagent.

Drop Technique for Carrying Out the Reaction

The titanium-chromotropic acid complex is only weakly fixed by filter paper, and as a result it is easily washed off by plain water, while decolorization of the spot occurs. It is more convenient to use the drop technique on cellophane. For this purpose the cellophane is given a preliminary treatment in the course of 1 hour with 10% alkali at 50°. The cellophane, when treated in this way, is easily colored by the reagent mixture consisting of the following components: 1 ml 0.01 mol/liter titanium sulfate, 1 ml of 0.01% methylene blue, and 0.01 g chromotropic acid (added in the dry state so as not to dilute the solution). The cellophane is immersed in this solution for 5-8 minutes and then withdrawn; drops of liquid are removed with a filter paper, and the cellophane dried in the air. Cellophane test papers can be stored for several months in a closed vessel in the dark.

The cellophane test paper has a reddish-brown color; if a drop containing fluoride ion is placed on it, a blue spot appears. It should be noted that the chromotropic acid complex, though only slowly, is nevertheless eventually washed off the cellophane by water. Therefore, if the change in color of the spot takes a long time (20 minutes and more) the reaction cannot be regarded as conclusive. The sensitivity of the reaction is 1 µg and the limiting dilution 1:50,000.

Effects of Other Ions

Sulfates, even in large amounts do not interfere. Phosphates cause a change in the color of the reagent in the same way as fluorides; nevertheless, the change as the result of phosphate action is much slower. It was established that 0.01 mol/liter of a phosphate solution in the course of 5 minutes decolorizes the reagent mixture to the same extent as 0.001 mol/liter sodium fluoride solution.

The sensitivity of the titanium-chromotropic acid reagent towards silicofluorides (fluosilicic acid and silico tetrafluoride) is the same as to the fluorides.

SUMMARY

1. A new color reaction for the fluoride ion is proposed which is based on the use of a titanium-chromotropic acid complex, and by means of which 0.2-2 mg/liter of fluoride ion can be detected.

2. The reaction can be carried out by a drop technique on cellophane. The sensitivity is 1 µg of fluoride ion at a limiting dilution of 1:50,000.

3. The reaction can be carried out in the presence of large amounts of sulfate, but in the presence of phosphates the reaction is not reliable.

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QUANTITATIVE ANALYSIS OF GLASSES OF THE SYSTEM $Na_2O - CaO - SiO_2$ ON THE BASIS OF THEIR PHYSICO-CHEMICAL PROPERTIES

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In our article on "Quantitative Analysis on the Basis of the Physico-Chemical properties of the Components" [1] we aimed at indicating the possibility of quantitative physico-chemical analysis of the components of this system, in which we confined ourselves to introducing one interpolated equation embracing a family of curves depending on one parameter for each property. In this way the problem resolved itself into a solution of linear equations.

In the present article in order that the practical side may be simplified we propose a graphical representation of the individual properties (Figs. 1 and 2), so that composition can be determined from a consideration of the points of intersection of lines representing equal properties.

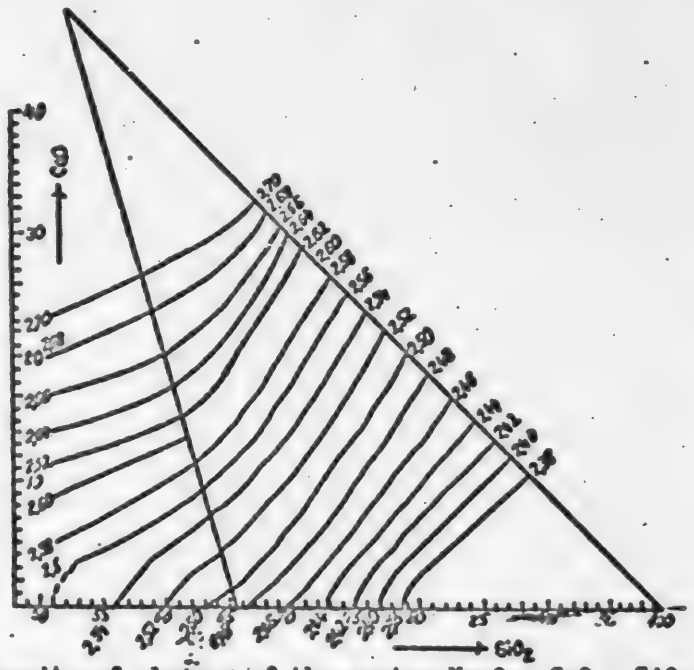

Fig. 1. Density of glasses of the system $Na_2O - CaO - SiO_2$. (wt.%).

[1] Proceedings of the Commission on Analytical Chemistry, Vol.8, 1952

Thus on one triangular diagram we plot softening temperatures and refractive indices and on the other the specific gravities for the same compositions; the point of intersection can be found by superposing transparent paper copies of the two diagrams on each other. In order to widen the scope and increase the accuracy of the analysis, we used 8 interpolated equations as the basis of our calculations for the families of curves corresponding to these three properties.

It should be noted that if the experimental results used as the basis of calculations are not reliable enough in some cases it might be necessary to resort to the method of least squares for calculation.

As examples we adduce comparisons of the compositions as determined by analyses with those calculated on the basis of physico-chemical properties. Results are given in tabular and graphical form.

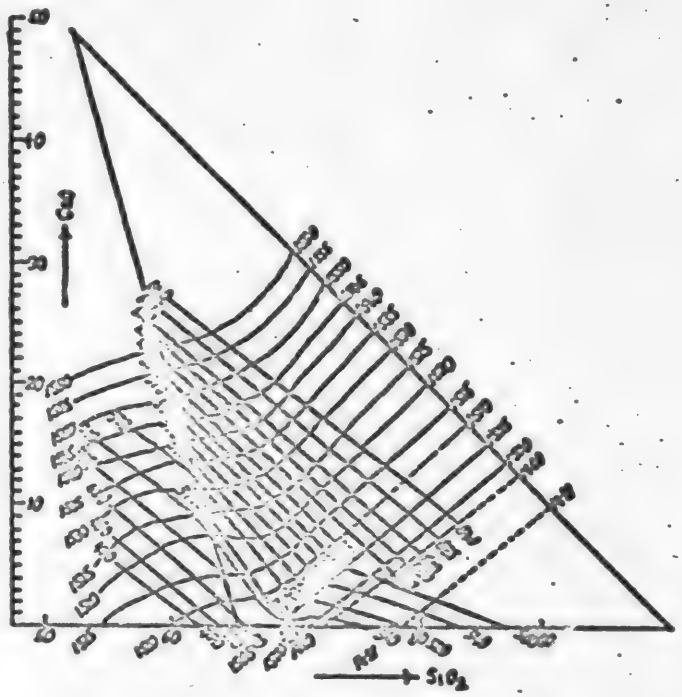

Fig.2. Refractive indices and softening temperatures of the glasses of the system Na_2O – CaO – SiO_2 (wt. %).

TABLE

Analyzed composition in percent		Physico-chemical constants of the composition Na_2O, CaO, SiO_2.	Components in percent calculated on the basis of:		
			n and t	n and d	average composition
Na_2O	22.5		22.0	23.1	22.6
CaO	9.5		9.6	9.2	9.4
SiO_2	68		68.4	67.7	68
		n=1.523; t=560° d=2.533			
Na_2O	16.4		17.4	16	16.7
CaO	3.3		2.8	3.6	3.2
SiO_2	80.3		79.8	80.4	80.1
		n=1.4935; t=560° d=2.3885			
Na_2O	15.2		15.5	14.7	15.1
CaO	10.7		11	10.3	10.7
SiO_2	74.1		73.5	75	74.2
		n=1.5182 t=600° d=2.4935			
NaO_2	15.2		16.1	14.1	14.9
CaO	9.3		9.2	10.1	9.6
SiO_2	75.5		74.7	75.8	75.3
		n=1.5135; t =.600 d=2.4734			
Na_2O	21.2		21.1	21.8	21.5
CaO	14.6		14.1	14.2	14.1
SiO_2	64.2		64.8	64	64.4
		n=1.536; t=570° d=2.5851			
Na_2O	21.7		21.5	21.8	21.8
CaO	11.8		11.8	11.7	11.7
SiO_2	66.5		66.5	66.5	66.5
		n=1.529; t=560° d=2.5564			
Na_2O	23		23.8	22.6	23.1
CaO	6.6		6.2	6.7	6.4
SiO_2	70.5		70	70.7	70.4
		n=15145; t=545° d=2.498			
Na_2O	37.5		37.1	37.9	37.5
CaO	5.8		6.2	5.9	6
SiO_2	56.7		56.7	56.2	56.5
		n=15238; t=480° d=2.572			
Na_2O	34		33.6	33.4	33.5
CaO	9.8		10	10.1	10
SiO_2	56.2		56.4	56.5	56.5
		n=15320; t=495° d=2.5976			

TABLE (Continued)

Analyzed composition in percent		Physico-chemical constants of the composition Na_2O, CaO, SiO_2.	Components in percent calculated on the basis of:		
			n and t	n and d	average composition
Na_2O	17.8		17.2	18.2	17.7
CaO	16		16.3	16	16.1
SiO_2	66.2		66.5	65.8	65.2
		n=1.540; t=595° d=2.591			
Na_2O	20		19.7	20.2	19.9
CaO	20		20	20	20
SiO_2	60		60.3	59.8	60.1
		n=1.5535; t=580° d=2.657			
Na_2O	12.3		12.3	10.4	11.2
CaO	13.1		13.1	14.6	13.6
SiO_2	74.7		74.7	75.5	75.2
		n=1.5211; t=627° d=2.496			

SUMMARY

1. The practice of quantitative physico-chemical analysis can be considerably simplified by graphical representation of individual properties.

2. The accuracy of the analysis of the components of a complex system can be considerably increased by increasing the number of the interpolated equations.

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THE QUANTITATIVE DETERMINATION OF TRIVALENT IRON BY MEANS OF TETRABORATE

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Existing methods for the quantitative determination of trivalent iron for the most part consist essentially in reducing it to the bivalent stage when it is titrated with different oxidizing agents [1,2,3,4].

Very little light has been thrown on the direct determination of trivalent iron [5,6]. The development of a direct method is a very important practical problem.

Shchigol's investigations have shown that soluble salts of aluminum, chromium and other elements react easily and quantitatively with the tetraborate ion to form new complex compounds of the composition $[MeB_4O_7]^+$ or $[Me(BO_2)_2B_2O_3]$ and $[Me_2(B_4O_7)_3]$ or $[Me_2(BO_2)_6 \cdot 3B_2O_3]$. We found that ferric ions in dilute solutions also react quantitatively with tetraborate to form similar complex iron borates.

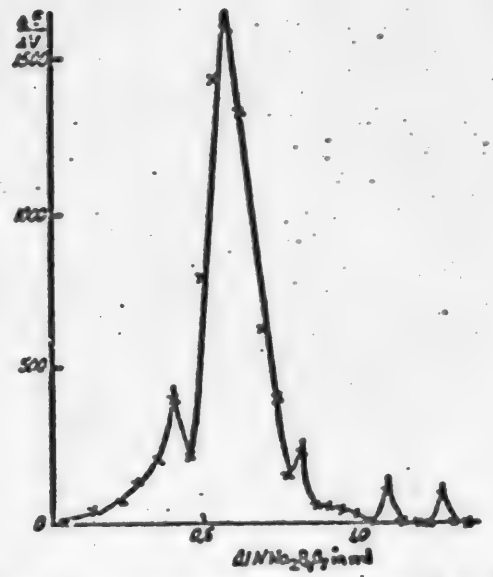


Fig. 1. Titration of 1 ml 0.057 N $FeCl_3$ with 0.1 N $Na_2B_4O_7$.

During the potentiometric titration of aqueous solutions of ferric chloride, the brown titration mixtures gradually acquire a yellow-orange color. One drop in excess of borate after the equivalence point leads to the formation of a precipitate which is obviously the result of the break down of a complex. A number of potential jumps are observed on the titration curve (Fig.1) the first – a small one – represents a compound in which 1 g-ion of iron corresponds to 1 g-ion of tetraborate $[FeB_4O_7]^+$, the second – a large one – is of practical significance and represents an equivalence point at which 2 g-ion of iron corresponds to 3 g-ion of tetraborate $[Fe_2(B_4O_7)_3]$ $\left(E_{Fe} = \frac{M}{3}\right)$. The reaction proceeds according to the following equation.

$$2Fe^{3+} + 3B_4O_7^{2-} \rightleftarrows [Fe_2(B_4O_7)_3].$$

The third, fourth, and fifth potential jumps indicate a gradual break down of the complex compound with the formation of basic salts and finally of ferric hydroxide. According to the extent of the decrease in concentration of the titrated iron salt the jump increases.

It is pertinent to speculate on the nature of these potential jumps after the equivalence point.

In order to answer this question the following experiments were carried out; 2 ml of 0.08 N $FeCl_3$ solution was placed in a 25 ml standard flask and 10 ml water and 1.6 ml of 0.1 N $Na_2B_4O_7$ solution added. The mixture was heated on a water bath until a completely clear solution was obtained. On cooling, an excess of borate was added; for the first experiment $^1/_3$ of the initial amount of borax was added (0.52 ml of the 0.1 N solution, i.e., $^1/_3$ of 1.6 ml); for the second $^2/_3$ (1.04 ml); and for the third $^3/_3$ (1.6 ml). The respective solutions were then made up to the mark with water and filtered. 10 ml of the filtrate in the presence of the same volume of glycerol was titrated with 0.1 N NaOH using phenolphthalein as indicator. The results of some of these experiments are given in Table 1.

TABLE 1

$FeCl_3$	Amount of 0.1 N solution taken, in ml		0.1 N NaOH, in ml		Amount, in ml, of 0.1 N BO_2 in the basic salt	Number of BO_2 groups in basic salt
	$Na_2B_4O_7$ initial	$Na_2B_4O_7$ excess	Reqd.	Excess		
1.6	1.6	0.52	3.72	3.30	0.42	2
1.6	1.6	1.04	4.24	3.96	0.28	1
1.6	1.6	1.5	4.8	4.73	0.07	-
4.0	4.0	1.34	9.34	8.04	1.3	2
4.0	4.0	2.68	10.68	10.12	0.56	1
4.0	4.0	4	12	11.90	0.1	-
1.6	1.6	3.2	6.4	6.1	0.3	1

On the basis of these results the number of BO_2^- groups in the basic salt can be calculated. Thus in the first experiment for each BO_2^- group 0.266 ml of 0.1 N NaOH was required (1.6 ml of 0.1 N $Na_2B_4O_7$ is equivalent to 3.2 ml of 0.1 N BO_2^-; each BO_2^- group = 3.2/12 = 0.266 ml 0.1 N NaOH). Thus in the first experiment two BO_2^- groups enter into the composition of the basic iron salt, while in the second, one BO_2^- group is involved. The equations for these reactions can therefore be represented as follows:

$$[Fe_2(B_4O_7)_3] + B_4O_7^{2-} + 8H_2O \longrightarrow Fe\begin{matrix}(BO_2)_2\\OH\end{matrix} + Fe(OH)_3 + 2BO_2^- + 12HBO_2;$$

(3rd jump on the curve in Fig.1)

$$[Fe(BO_2)_2OH] + B_4O_7^{2-} + 2H_2O \longrightarrow Fe(BO_2)(OH)_2 + 2BO_2^- + 3HBO_2;$$

(4th jump)

$$[Fe(BO_2)(OH)_2] + B_4O_7^{2-} + 2H_2O \longrightarrow Fe(OH)_3 + 2BO_2^- + 3HBO_2.$$

(5th jump)

The last experiment shows that ferric hydroxide reacts with boric acid to form a basic salt possibly as follows:

$$2Fe(OH)_3 + B_4O_7^{2-} \longrightarrow Fe(OH)_3 \cdot Fe(BO_2)(OH)_2 + 2BO_2^- + HBO_2.$$

It should be pointed out that the basic borates of iron were synthesized and studied by Rose [7]; he ascribed to them the formulas $4Fe_2O_3 \cdot 3B_2O_3 \cdot 9H_2O$ or $6Fe(BO_2)(OH)_2 \cdot 2Fe(OH)_3$. In addition the basic borates occur in nature as minerals

such as fonsenite $Fe_2O_3 \cdot B_2O_3$ and also enter into the composition of Inderak borates which are found in the USSR.

In order to study the complex iron borates further these salts were potentiometrically titrated with 0.1 N HCl and $H_2C_2O_4$ in aqueous alcohol. The titration is represented in Fig.2. When HCl is used, 3 potential jumps can be observed on the titration curve according to the number of B_4O_7 groups composing the internal sphere of the complex. The reaction proceeds as follows:

$$[Fe_2(B_4O_7)_3] + 2HCl + 5H_2O \longrightarrow [Fe_2(B_4O_7)_2Cl_2] + 4H_3BO_3,$$

$$[Fe_2(B_4O_7)_2Cl_2] + 2HCl + 5H_2O \longrightarrow [Fe_2(B_4O_7)Cl_4] + 4H_3BO_3,$$

$$[Fe_2(B_4O_7)Cl_4] + 2HCl + 5H_2O \longrightarrow [Fe_2Cl_6] + 4H_3BO_3.$$

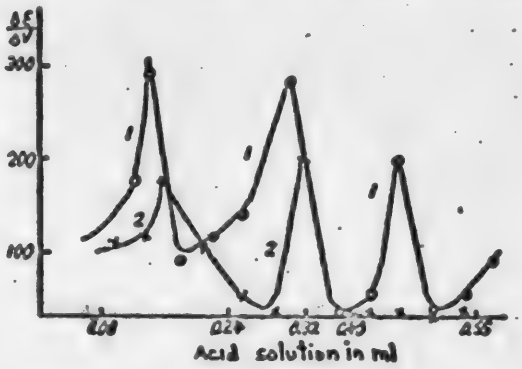


Fig.2. Titration of 1 ml 0.048 N complex with 0.1 N HCl (Curve 1); the same with 0.094 N $H_2C_2O_4$ (Curve 2).

When oxalic acid is used for titration, only two jumps are observed. The third jump is absent. This may be explained if it is assumed that $[Fe_2(B_4O_7)_3]$ is a multinuclear complex compound $[FeB_4O_7]\,[Fe(B_4O_7)_2]$. Obviously in this case only two so called "anionic" groups of $B_4O_7^{2-}$ are titrated; the cationic group $B_4O_7^{2-}$ does not titrate since in all probability the instability constant of $[Fe(B_4O_7)]^+$ is less than or equal to that of $[FeC_2O_4]^+$.

In order to determine the instability constant of the iron borates we studied the equilibrium in the systems $[Fe_2(B_4O_7)_3]$ – KSCN and $[Fe_2(B_4O_7)_3]$ – CH_3COONa. The instability constants for $[FeCNS]^{++}$ and $\left[Fe\begin{matrix}Ac_2\\ \\ H_2O\end{matrix}\right]^+$ have been determined by Babko [10,12]. This in conjunction with the experimentally determined equilibrium constant enables the instability constants of the iron borates to be calculated.

$$K_p = \frac{K^2[FeCNS]^{2+}}{K[Fe_2(B_4O_7)_3]}.$$

The average value of $K[Fe_2(B_4O_7)_3]$ is $0.7 \cdot 10^{-12}$, while $K[FeB_4O_7]^+ = 1.78 \cdot 10^{-17}$.

Of a number of other physico-chemical methods of investigating complex compounds in solution we used the cryoscopic and specific electro-conductivity methods for the system $FeCl_3$ – $Na_2B_4O_7$.

Cryoscopy as a physico-chemical method of analysis was proposed by Fialkov and Muzika [8] and is based on the fact that in a system where complex formation occurs, the amount of particles in solution is not additive, but depends on the

composition and properties of the complex. The change in the number of particles as a result of the formation of a new compound should be reflected in the extent of the depression. Aqueous solutions of the $FeCl_3$ – $Na_2B_4O_7$ system were subjected to test. The procedure was as follows: to an aquous solution of $FeCl_3$ was added a gradually increasing amount of borax and the freezing point determined. The Beckmann method was used. Since on interaction of $FeCl_3$ and $Na_2B_4O_7$ an equivalent amount of NaCl is formed which affects the freezing point of the system, preliminary freezing point measurements were made on aqueous solutions of the system $FeCl_3$ – NaCl where the variable was NaCl. Results are given in Table 2 and Fig. 3.

TABLE 2

Weight in g				$Na_2B_4O_7$ $FeCl_3$ in mol.	t_0	t_1	t_2	t_3	Δt
H_2O	$FeCl_3$	NaCl	$Na_2B_4O_7$						
50.03	0.162	–	–	–	3.58	3.43	–	–	–
50.03	0.162	0.0117	0.02013	0.1	3.58	3.43	3.415	3.39	0.025
50.03	0.162	0.0234	0.04025	0.2	3.58	3.43	3.400	3.36	0.040
50.03	0.162	0.0351	0.06037	0.3	3.58	3.43	3.885	3.34	0.045
50.03	0.162	0.0468	0.08050	0.4	3.58	3.43	3.370	3.33	0.040
50.03	0.162	0.0585	0.1006	0.5	3.58	3.43	3.335	3.31	0.045
50.03	0.162	0.0702	0.1208	0.6	3.58	3.43	3.340	3.29	0.050
50.03	0.162	0.0819	0.1409	0.7	3.58	3.43	3.325	3.28	0.045
50.03	0.162	0.0936	0.1610	0.8	3.58	3.43	3.310	3.26	0.050
50.03	0.162	0.1053	0.1812	0.9	3.58	3.43	3.295	3.24	0.055
50.03	0.162	0.1170	0.2014	1	3.58	3.43	3.280	3.21	0.070
50.03	0.162	0.1287	0.2215	1.1	3.58	3.43	3.260	3.20	0.060
50.03	0.162	0.1404	0.2416	1.2	3.58	3.43	3.250	3.17	0.080
50.03	0.162	0.1521	0.2617	1.3	3.58	3.43	3.235	3.15	0.085
50.03	0.162	0.1638	0.2818	1.4	3.58	3.43	3.220	3.13	0.090
50.03	0.162	0.1696	0.2919	1.45	3.58	3.43	3.210	3.13	0.080
50.03	0.162	0.1725	0.2970	1.47	3.58	3.43	3.205	3.13	0.075
50.03	0.162	0.1842	0.3171	1.57	3.58	3.43	3.420	3.13	0.297

Notes.
t_0 – freezing point of water
t_1 – freezing point of an aqueous solution of $FeCl_3$
t_2 – freezing point of an aqueous solution of the system $FeCl_3$ – NaCl
t_3 – freezing point of aqueous solution of the system of $FeCl_3$ – $Na_2B_4O_7$
Δt – depression of the complex ($t_2 - t_3$)

The results obtained show that two minima are observed on the depression curve which correspond to molar ratios of $FeCl_3$:$Na_2B_4O_7$=1:1 and 1:1.5, which confirms the formation in solution of complex borates of the compositions $[FeB_4O_7]^+$ and $[Fe_2(B_4O_7)_3]$.

Measurements on the specific electroconductivity of the system were carried out at 25 and 40° in a concentration range of from 0 to 61.4 mol. % borax. For this purpose a series of solutions was prepared in which gradually increasing amounts of borax (from $2 \cdot 10^{-3}$ to $2 \cdot 10^{-2}$ mol/l) were added to a constant amount of $FeCl_3$. The specific electroconductivity of equivalent amounts of NaCl formed by the interaction of $FeCl_3$ and $Na_2B_4O_7$ was taken into account. Results are given in Table 3 and Fig 4. These physico-chemical investigations of the system $FeCl_3$ – $Na_2B_4O_7$ show convincingly that ferric ions in aqueous solutions react with the tetraborate ion to form multi-nuclear complex compounds of the composition $[FeB_4O_7]^+$ or $[Fe(BO_2)_2B_2O_3]^+$ and $[Fe_2(B_4O_7)_3]$ or $[Fe_2(BO_2)_6 \cdot 3B_2O_3]$.

This served as a basis for developing a new method for the quantitative determination of ferric ions both in the free state or in admixture with other ions.

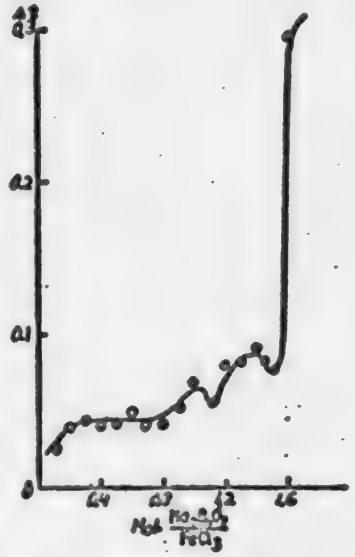


Fig. 3. Cryoscopy of the $FeCl_3 - Na_2B_4O_7$ system.

Fig. 4. Specific electroconductivity of the $FeCl_3 - Na_2B_4O_7$ system.

TABLE 3

$Na_2B_4O_7$, in mol. %	$x \cdot 10^3$ at 25°			$x \cdot 10^3$ at 40°		
	$FeCl_3 - Na_2B_4O_7$	NaCl	Complex	$FeCl_3 - Na_2B_4O_7$	NaCl	Complex
–	5.39	–	–	6.50	–	–
22.4	6.31	0.927	5.38	7.12	1.35	5.77
30.3	5.87	1.3	4.57	7.12	1.74	5.38
36.7	5.75	1.84	3.91	6.92	2.18	4.74
42.0	5.32	2.23	3.09	6.67	2.80	3.87
46.5	5.309	2.64	2.68	6.52	3.17	3.35
50.3	5.053	3.17	1.98	6.07	3.78	2.29
53.6	4.50	3.40	1.10	5.51	4.22	1.29
57.1	4.20	4.00	0.20	4.84	4.60	0.24
59.9	4.50	4.37	0.17	5.40	5.43	0
61.4	4.60	4.65	0	5.50	5.60	0

The choice of an indicator electrode plays an important role in the potentiometric method for the determination of ferric iron described below. A platinum plate covered with a thin layer of platinum black serves as the electrode. This electrode obviously plays the part of an incompletely reversible oxygen electrode. After a preliminary cleaning of the electrode with emery paper it is placed in a 1% solution of chloroplatinic acid and platinized in the normal fashion for 15-20 seconds. If the platinization time is extended a thick layer of platinum black forms on the electrode and the potential on such an electrode is established only

very slowly. The electrode is finally washed with water, and then subjected to cathodic polarization for removal of adsorbed chloride by placing it in a 1 N ammonia solution. After 15-20 seconds the electrode is carefully washed, first with warm and then with cold water. The electrode can be used the day after platinization. It should be kept in water, where it remains sensitive for a long time.

A series of ferric chloride solutions of various concentrations (0.06-0.008 N) was prepared for investigation. They were standardized by duplicate gravimetric and volumetric determinations. A 0.1 N solution of sodium borate was used as the standard titrant.

Experimental Procedure. 0.25-2 ml of 0.06 N $FeCl_3$ solution diluted with 25 ml of water in a 200 ml beaker was titrated potentiometrically with 0.1 N borax in the presence of the indicator electrode. A saturated calomel electrode was used as the standard electrode. A galvanometer with a sensitivity of 10^{-7}A was used as the null instrument. The electrode potential during titration was established within 1-2 minutes after each addition of borax solution. The potential change of the electrode is determined on the one hand by a decrease in the hydrogen ion concentration of the solution during the titration of ferric chloride with borax, and on the other hand by the formation of the iron borates which only dissociate slightly. The change in $\Delta E/\Delta V$ during titration is shown in Fig. 5. Completely satisfactory results were obtained (Table 4).

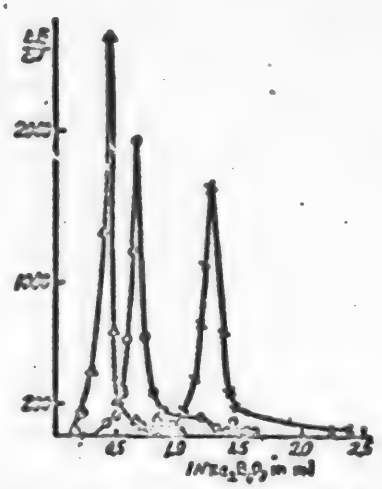


Fig. 5 Titration of 0.053 N $FeCl_3$ with 0.1 N $Na_2B_4O_7$. × = 2 ml; O = 1 ml; Δ = 0.5 ml.

The mean error of a determination for an iron concentration of the order of $2 \cdot 10^{-3}$ g is 0.1%. For lower concentrations of iron of the order of $3 \cdot 10^{-4}$ g the titration error amounts to 2%.

Determination of Ferric Ions in the Presence of Acids

By means of the method proposed ferric ions can be determined not only in neutral solution, but also in acid solution. In this case two potential jumps are observed: the first–a small one–indicates the end of the titration of the free acid and the second– a large one–the end of the titration of the sum of the acid and ferric ions (Fig. 6, Curve 1). The small value of the first jump on the titration curve can be explained by the fact that the drop of borax added in excess after the first equivalence point has little effect on the electrode potential, since the iron borate which is formed only dissociates very slightly. Naturally in order to get a more marked potential jump during the titration of the acid in solution it is essential that the ferric ions should be bound in a more stable complex than ferric tetraborate.

$C_2O_4^{2-}$ ions are the most suitable for this purpose since they form a complex $[Fe(C_2O_4)_3]^{3-}$ with iron, the instability constant of this complex being $1.2 \cdot 10^{-24}$ [9] (Fig. 6, Curve II).

Experimental Technique. To a known volume of a mixture of a ferric salt and acid is added 1.5-2 g of dry sodium oxalate. The mixture is shaken up and diluted to 50 ml with water, after which it is titrated with 0.1 N borax potentiometrically (the free acid in solution is also determined by this method).

TABLE 4

Fe taken, g·10³	Fe found, g·10³	Interval drop, in mV	Error, g·10³
2.376	2.378	602-538	+0.002
1.188	1.188	613-525	-
0.594	0.594	614-493	-
0.336	0.339	580-463	-0.007

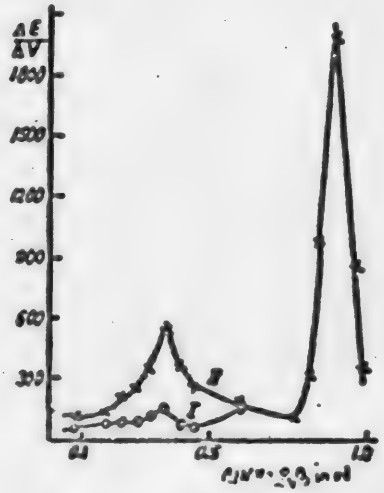


Fig. 6 Titration of free acid in a mixture of 1 ml 0.0343 N $FeCl_3$.
Curve 1) without $Na_2C_2O_4$
Curve 2) with $Na_2C_2O_4$.

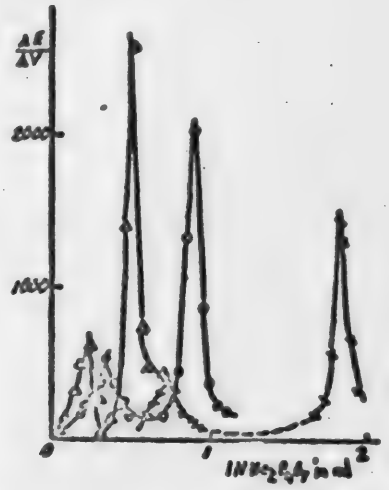


Fig. 7 Titration of 0.057 $FeCl_3$ in an acid medium.
× – 2 ml; O – 1 ml; Δ – 0.5 ml

A similar volume of the mixture (i.e. the original volume before dilution to 50 ml) is diluted to 25 ml with water and potentiometrically titrated against 0.1 N borax for the total hydrogen ions and ferric ions. The amount of iron is found by difference.

The concentration of the free acid in solution can also be determined by titration against 0.1 N NaOH in the presence of the same amount of sodium oxalate and with phenolphthalein as indicator.

The results are given in Table 5 and Fig. 7.

TABLE 5

Amount taken, in g·10³		Amount found, in g·10³		Error, in g·10³
HCl	Fe^{3+}	HCl	Fe^{3+}	
2.657	2.048	2.664	2.037	-0.011
1.328	2.024	1.332	1.019	-0.005
0.664	0.512	0.664	0.510	-0.002
0.332	0.256	0.333	0.254	-0.002
1.328	0.256	1.334	0.254	-0.002

Determination of Ferric Ions in the Presence of Other Ions

1. By means of the method described it is possible to determine iron in solutions of various complex compounds. The nature of many complex compounds in solution and their instability constants have been studied by Babko [10-14]. We have studied the potentiometric determination of iron by tetraborate in solutions of:

acetates, salicylates, thiocyanates, and fluorides. For this purpose known amounts of sodium acetate, salicylate, and fluoride, respectively, and potassium thiocyanate sufficient for the formation of the respective complex iron salts were added beforehand to a known amount of ferric salt solution. The complex compounds formed were then potentiometrically titrated with 0.1 N borax, as described previously.

Results of these determinations are given in Table 6.

2. The determination of iron in the presence of copper is of practical significance.

While ferric ions form soluble compounds with $B_4O_7^{2-}$ ions, cupric ions give an insoluble hydroxide. If both ferric and cupric ions are present together then the cupric ions will be titrated first and the ferric ions afterwards.

TABLE 6

No. of Expt.	Composition of the mixture	Amount taken in $g \cdot 10^3$	Amount found in $g \cdot 10^3$	Error in $g \cdot 10^3$
1	$FeCl_3$ CH_3COONa	1.229 328.0	1.231 –	+0.002 –
2	$FeCl_3$ KCNS	1.229 5.4	1.231 –	+0.002 –
3	$FeCl_3$ SalNa	0.912 19.2	0.894 –	−0.018 –
4	$FeCl_3$ NaF	1.08 8.4	1.08 –	– –
5	$FeCl_3$ $CuSO_4$	1.08 33.6	1.08 –	– –
6	$FeCl_3$ $CuSO_4$	1.974 2.924	1.974 2.861	– −0.063
7	$FeCl_3$ $CuSO_4$ HCl $Na_2C_2O_4$	1.862 2.924 2.430 2000.0	– – 2.419 –	– – −0.011 –
8	$FeCl_3$ $CuSO_4$ HCl	1.862 2.924 2.43	1.862 2.980 –	– −0.056 –
9	$FeCl_2$ $NiCl_2$, $CoSO_4$ Na_2WO_4 $(NH_4)_2MoO_4$ NH_4VO_3 SalNa	1.045 0.1 0.1 N 200.0	1.036	−0.009
10	$FeCl_3$ NiCl2, $CoSO_4$, Na_2WO_4, $(NH_4)_2MoO_4$, NH_4VI_3, KCl, SalNa	1.045 2.430 200.0	0.070	+0.035

When copper ions are titrated in neutral media (Fig. 8), an increase in the potential jump is observed with decreasing salt concentration.

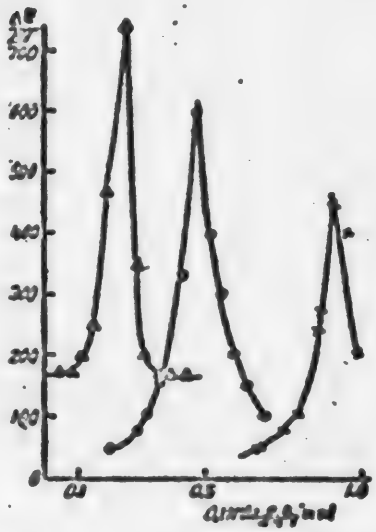


Fig. 8 Titration of 0.046 N $CuSO_4$ with 0.1 N $Na_2B_4O_7$
x - 2 ml; O - 1 ml; Δ-0.5 ml.

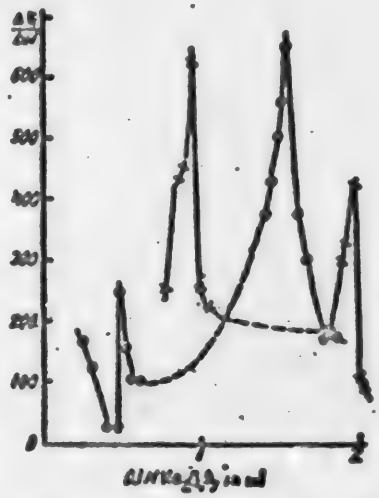


Fig. 9 Titration of 0.046 N $CuSO_4$ and 0.053 N $FeCl_3$ together with 0.1 N $Na_2B_4O_7$
x - 2 ml $FeCl_3$+2 ml $CuSO_4$
O - 2 ml $FeCl_3$+1 ml $CuSO_4$.

During the titration of ferric and cupric ions when present together two potential jumps are observed on the titration curve; the first indicates the end of the titration for cupric ions and the second indicates the end of the titration for the sum of cupric and ferric ions. The amount of iron is thus found by difference. It should be noted that as the amount of copper decreases and the amount of iron increases the first potential jump decreases, while the second, the sum of the two, increases (Fig. 9).

For the determination of ferric iron and copper in acid media the concentration of the free acid in solution must be preliminarily determined by an independent titration in the presence of oxalate ions as shown above.

In the second titration the concentrations of acid, cupric and ferric ions are all determined simultaneously. In this case the first potential jump on the titration curve corresponds to the end of the titration for the sum of acid and copper. The difference between this volume of borax and that used for neutralization of the acid (first titration) gives the amount of copper. The second potential jump on the titration curve corresponds to the total acid, ferric and cupric ions. The amount of iron is found by difference.

Results are given in Table 6.

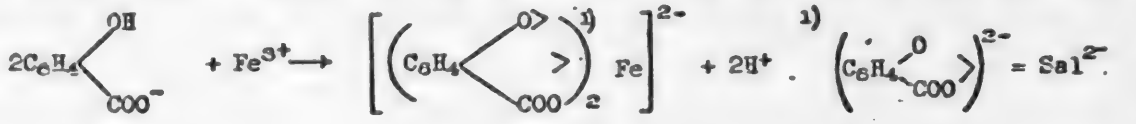
3. The determination of ferric iron in the presence of soluble salts of nickel, cobalt, vanadium, molybdenum, and tungsten is of great interest.

During the titration of such a system with borax, the nickel and cobalt ions behave similarly to the cupric ions and separate out as basic salts and hydroxides

and mask the fundamental iron titration. On addition to such a solution of some salicylate ions which form a stable complex with iron, the iron complex is first titrated with borax. To a solution of the mixture containing 1-2 ml of 0.05-0.06 N $FeCl_3$ and 0.1 ml each of approximately 0.1 N solutions of nickel, cobalt, molybdenum, vanadium and tungsten respectively, 0.2-0.3 g of sodium salicylate is added and the whole diluted to 50 ml with water prior to potentiometric titration with 0.1 N borax.

Molybdates, tungstates, and vanadates form slightly soluble compounds with ferric ions. In the presence of a sufficient amount of salicylate ions these precipitates do not settle out, because of the formation of a very stable complex of ferric salicylate in solution ($K \approx 4 \cdot 10^{-7}$).

Two potential jumps (Fig. 10) are observed on the titration curve; the first - a large one - indicates the end of the titration for free acid formed as the result of the interaction of ferric ions with sodium salicylate according to the equation:



The second jump, which is not so pronounced, corresponds to the formation in all probability of a mixed complex compound.

$$FeSal_2 + B_4O_7^{2-} \rightleftharpoons [FeSalB_4O_7] + Sal^{2-}$$

The iron content is calculated from the first potential jump (Fig. 10). In this way iron can be determined not only in neutral mixtures but in solutions containing hydrochloric acid.

The experimental results obtained, which are completely satisfactory, are shown in Table 6.

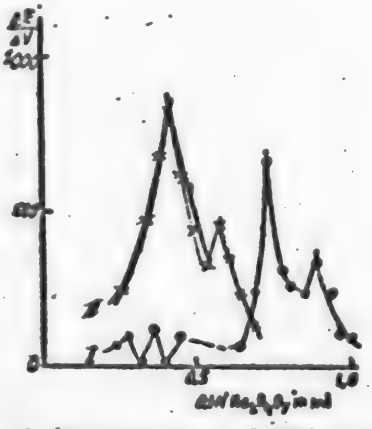


Fig. 10. Titration of 0.053 $FeCl_3$ with 0.1 N borax in the presence of other ions. II) In neutral media; I) in acid media.

Determination of Iron in Ores and Other Materials

The potentiometric method described above for the determination of ferric ions can be successfully applied to the determination of iron in various materials containing it, such as ores, coal, dolomite, etc.. In these cases 0.03-0.04 g of the well-ground substance is calcined for 10 minutes with ten times its weight of anhydrous sodium carbonate until a homogenous mass is obtained. The melt is worked up with 2-3 ml of concentrated hydrochloric acid until the whole goes into solution. (disappearance of black specks). The solution is then cooled and diluted with water to 100 ml in a standard flask. Free acid is determined in one aliquot as follows; to 10 ml of solution, 1 g of $Na_2C_2O_4$ is added. the solution diluted to 50 ml with water and titrated with 0.1 N alkali using phenolphthalein as indicator. In the second aliquot total acid plus iron is determined potentiometrically with 0.1 N borax.

The iron is calculated by difference.

The iron was determined in the same materials by another method, the iodometric method, as a check. Results are given in Table 7.

TABLE 7

Test material	Wt. in g[1]	Found		
		potentiometrically		iodometrically
		in g	in %	in %
Hornstone magnetite-aegirite	0.0294	0.01075	36.55	36.48
Hornstone schistous	0.0438	0.0207	47.30	47.25
Martite ore	0.0320	0.0238	74.62	74.60
Stone coal, Sample 1	0.0494	0.01758	35.40	35.25
Stone coal, Sample 2	0.1810	0.0152	8.40	8.25
Brown coal	0.6046	0.021	3.46	3.32
Lignite	0.0480	0.0030	6.3	6.3
Dolomite	0.3094	0.0028	0.905	0.89
Limestone	1.0010	0.00011	0.011	0.009
Kaolin	0.478	0.00153	0.320	0.28

[1] The weight of ash is given for the coal.

This method was also used by us successfully for the determination of iron in blood, medicinal preparations, and water.

SUMMARY

1. As a result of physico-chemical research it was established that ferric ions interact with tetraborate ions in solution to form a number of new complex iron borates.

2. On this basis a direct method for macro and micro potentiometric determinations of ferric iron both in neutral and acid media has been developed.

3. By this method iron can be determined in the presence of copper, nickel, cobalt, vanadates, molybdates, tungstates, etc.

4. This method can be used for the determination of iron in ores and other materials containing it.

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NEW VOLUMETRIC AND GRAVIMETRIC METHODS FOR THE DETERMINATION OF CADMIUM

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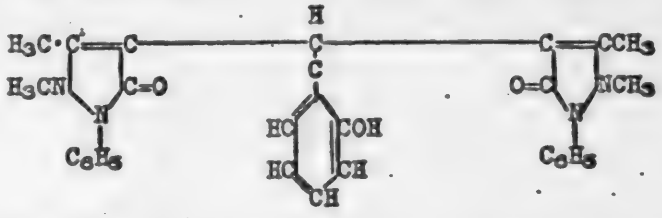
For the determination of cadmium in the presence of copper the poisonous and not always readily available potassium cyanide or brucine [1,2,3] are used. It has been shown recently that cadmium can be detected qualitatively by pyramidon in the presence of potassium iodide, and quantitatively by the antipyrine-bromide reagent [4] and by diantipyrylmethane. Hitherto very few methods have been described in the literature for the volumetric determination of cadmium; thus there is a reference to the possibility of titrating cadmium sulfide with iodine in acid solution; this method however does not give positive results because cadmium sulfide is contaminated with adsorbed salt [5]; Berg and Durn precipitated cadmium with β-naphthoquinoline in the presence of potassium iodide and the amount of iodine determined in the precipitate with potassium iodate [5]. The determination of cadmium with 8-hydroxyquinoline [6] is based on the bromometric titration of the oxine combined with the metal. As our investigations have shown, it is possible to determine cadmium quantitatively by means of diantipyrylorthohydroxyphenylmethane:



or $C_{21}H_{28}O_3N_4$ (Mol.wt. 480.55). Diantipyrylorthohydroxyphenylmethane exists in the form of long white needles which are soluble to the extent of 0.1% in water and 5.5% in alcohol[1]. In acid media cadmium forms a slightly soluble complex of the composition: $(C_{28}H_{28}O_3N_4)_2H_2[CdBr_4]$ with diantipyrylorthohydroxyphenylmethane in the presence of potassium bromide.

The reaction proceeds as follows:

$$2D + 4Br' + 2H^+ + Cd^{2+} = (D)_2H_2[CdBr_4]$$

(from here onwards diantipyrylorthohydroxyphenylmethane will be denoted by D). Cations of zinc, copper, cobalt, iron, aluminum, chromium and also of the alkali and alkaline earth elements do not form precipitates with D in the presence of bromine ions and consequently do not interfere with the determination of cadmium. Analysis of the crystalline precipitate formed during the determination of cadmium after recrystallization from aqueous alcohol and drying at 120° gave the following results: 0.2 g substance, AgBr 0.1144 g, $CdSO_4$ 0.031 g. Found Br 24.34%; Cd 8.35%.

For $[C_{28}H_{28}O_3N_4]_2H_2[CdBr_4]$ mol.wt. = 1395.18. Br calculated 22.91% and Cd 8.06%.

The volumetric method for the determination of cadmium is based on the action of alkali on the precipitate of $(D)_2H_2[CdBr_4]$, during which neutralization of

1) See reference H. Amal, Chem. Abs. 44, 6853 (1950).

TABLE 1

Property	$[C_{28}H_{28}O_2N_2]_2[CdBr_4]$
Color	Pale rose
Solubility in water at 15°	0.06:100
" in alcohol	0.45:100
" in ether	insoluble
Behavior of a saturated aqueous solution of the compound with dilute H_2SO_4 and HNO_3	unchanged
Ditto towards conc. H_2SO_4 and HNO_3	unchanged
" " 1 N NaOH	$Cd(OH)_2$ precipitated
" " $AgNO_3$	Pale yellow precipitate of AgBr formed
Behavior of dry solid on heating in a capillary	Melts at 193°, changes into a red liquid

hydrogen ions occurs. Determinations of cadmium were made initially on pure salts. The reagent is prepared as follows: 0.25 g of D is dissolved with slight heating in 25 ml ethyl alcohol and to the solution 25 ml of 1 N sulfuric acid and 25 ml of a 5% solution of potassium bromide added. Each 5 mg cadmium requires 20-25 ml of the reagent solution described for precipitation. At low concentrations of cadmium, supersaturated solutions are apparently formed, because in order to accelerate the formation of a precipitate it is necessary to stir the mixture with a glass rod. Turbidity develops either immediately or after some time and then a crystalline precipitate forms. After 1½ hours the precipitate is filtered through a No.4 glass crucible and washed with 10 ml of a dilute solution (1:4) of the reagent 3-4 times. The moist precipitate is then washed from the crucible with 30-35 ml of ethyl alcohol into a 300-350 ml flask. The liquid is gently heated in order to dissolve the precipitate, 150 ml of distilled water, 4-6 drops of methyl orange are added and the solution titrated with 0.1 N alkali, 1 ml of 0.1 N NaOH is equivalent to 5.62 mg cadmium.

Results are given in Table 2.

TABLE 2

Expt. No.	Vol. of $Cd(NO_3)_2$ solution	Amount of cadmium, in mg	0.1 N NaOH used, in ml	Cadmium found, in mg	Absolute error, in mg
1	1	5	0.812	4.56	-0.44
2	2	10	1.81	10.17	+0.17
3	2	10	1.82	10.23	+0.23
4	3	15	2.6	14.61	-0.39
5	3	15	2.69	15.12	+0.12
6	4	20	3.6	20.23	+0.23
7	4	20	3.6	20.23	+0.23
8	5	25	4.31	24.22	-0.78
9	6	30	5.33	29.93	-0.05
10	6	30	5.36	30.12	+0.12

Determination of cadmium in the presence of copper is carried out as follows: to the solution containing a known weight of cadmium is added up to 0.5 g of cupric chloride - $CuCl_2 \cdot 2H_2O$, and then the reagent solution, 20-25 ml for each 5 mg of cadmium. The method then follows the procedure outlined above. Results of the determinations are given in Table 3.

TABLE 3

Vol. of $Cd(NO_3)_2$, in ml	Amount of cadmium, in mg	Amount of $CuCl_2 \cdot 2H_2O$ added, in g	0.1 N NaOH used, in ml	Cd found, in mg	Absolute error, in mg
3	15	0.5	2.65	14.89	−0.11
3	15	0.5	2.68	15.06	+0.06
4	20	0.5	3.4	19.11	−0.89
4	20	0.5	3.45	19.4	−0.6

The volumetric method given for determining Cd was used for the analysis of various alloys to which cadmium had been added. Two alloys were chosen for analysis: iron-aluminum bronze containing Cu, Fe, Al, Mn and Zn, and electron metal containing mainly magnesium, and also Al (7.7%) and Zn (1.65%). 1 g of the bronze was dissolved in 10 ml dilute (1:1) nitric acid and the solution obtained evaporated on a water bath, when 50 ml of water was added. 0.5 g of electron was dissolved in 10 ml hydrochloric acid (1:5) and 50 ml water. The solutions should be clear. The procedure adopted subsequently was that described above. Results are given in Table 4.

TABLE 4

Vol. of solution, in ml	Amount of $CdSO_4$ solution added, in ml	Cd content, in mg	0.1 N NaOH used, in ml	Cd found, in mg	Absolute error, in mg
		Iron-Aluminum Bronze			
15	4	20	3.6	20.23	+0.23
20	5	25	4.52	25.4	+0.4
15	4	20	3.5	19.67	−0.33
		Electron metal			
25	4	20	3.55	19.95	−0.05
25	5	25	4.55	25.01	+0.01

These results show that Mg, Al, Zn, Fe and Cu do not interfere with the volumetric determination of cadmium and that despite the fact that the amounts of these elements are greatly in excess of that of cadmium, the relative experimental error varies within ±3%. For the gravimetric determination of cadmium the precipitate is filtered through a No.4 glass crucible, washed with dilute reagent solution first and then with a mixture of alcohol and ether (1:1), and dried at 110-120° to constant weight. The conversion factor to cadmium is 0.08057. Results are given in Table 5.

Cadmium can be determined in the presence of copper also gravimetrically. Results are given in Table 6.

Cadmium can be precipitated with D at higher concentrations of D, sulfuric acid and potassium bromide; e.g., the precipitating reagent can be prepared as follows: 0.5 g of D is dissolved in 50 ml 50% alcohol to which are added 25 ml of 2 N sulfuric acid and 25 ml 10% potassium bromide. The drawback of such a solution is that after 4-5 hours it deposits a precipitate; it is necessary therefore to precipitate cadmium with a warm solution of the precipitant and not to leave the precipitate for more than 1½ hours.

If these conditions are observed and the method above followed for the determination of cadmium, good results are obtained (Table 7).

TABLE 5

$Cd(NO_3)_2$ taken, in mg	Cd content, in mg	Wt of ppt., in g	Cd found, in mg	Absolute error, in mg
1	5	0.0626	5.04	+0.04
2	10	0.1272	10.25	+0.25
3	15	0.1910	15.39	+0.39
1	5	0.0640	5.16	+0.16
2	10	0.1286	10.36	+0.36
3	15	0.1906	15.36	+0.93

TABLE 6

$Cd(NO_3)_2$ taken, in mg	Cd content, in mg	$CuCl_2 \cdot 2H_2O$ added, in g	Wt. of ppt., in g	Cd found, in mg	Absolute error, in mg
1	5	1	0.0630	5.077	+0.077
2	10	1	0.1264	10.18	+0.18
3	15	1	0.1924	15.5	+0.5
3	15	0.5	0.1782	14.36	−0.64

TABLE 7

Vol. of $CdSO_4$ in ml	Amount of Cd, in mg	Wt. of ppt., in mg	Cd found, in mg	Absolute error, in mg
1	5	0.0616	4.96	−0.04
2	10	0.1214	9.78	−0.22
2	10	0.1234	9.94	−0.06
2.5	12.5	0.1536	12.38	−0.12
3	15	0.1850	14.91	−0.09
1.5	7.5	0.0954	7.69	+0.19
2.5	12.5	0.1568	12.64	+0.14
3	15	0.1896	15.28	+0.28

Cadmium was successfully determined gravimetrically in different alloys to which it had been added. In addition to the volumetric and gravimetric methods for the determination of cadmium, attempts were made to develop a colorimetric method by diazotization of the reaction product, but in view of the low sensitivity of the color obtained the method is of no significance.

SUMMARY

A new complex compound has been prepared $[DH]_2[CdBr_4]$ and some of its properties studied.

New volumetric and gravimetric methods have been developed for the determination of cadmium in the presence of magnesium, aluminum, zinc, copper and other metals.

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DETERMINATION OF CUPROUS OXIDE, CUPRIC OXIDE, AND METALLIC COPPER IN COPPER POWDERS

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One of the most difficult problems to solve in analytical chemistry is that of the determination of copper in its different forms. Information in the literature is very scanty.

Various methods have been proposed by Tananaev [1], Lavrukhina [2], Hard and Clerk [3] and other investigators for the extraction and determination of metallic copper and cuprous oxide in mixtures of Cu, Cu_2O, CuO. Of these methods Lavrukhina's method [2] gives the most satisfactory results.

Our problem was to work out an accurate method for the determination of cuprous oxide, cupric oxide, and metallic copper in copper powders. The copper powders which served as the object of our investigation and which were prepared by an electrolytic method are used to a considerable extent at present for the production of so-called self-lubricating bronze bearings. These bearings are produced by a metallo-ceramic process and have a composition similar to that of cast bronze bearings: they usually contain about 90% copper; 10% tin, and sometimes 1.5-4.5% graphite.

The industry which produces these self-lubricating bearings lays down certain specifications for the chemical composition of the copper powders. In the production of these powders therefore it is essential to be able to determine rapidly the metallic copper content and that of certain oxygen compounds of copper, viz., cupric and cuprous oxides. Up to the present, however, the possibility of carrying out such determinations has been small as far as information in the literature is concerned.

Method, Reagents, and Materials

N.A.Tananaev's investigations [1] were used as the basis for the method. Ammonium chloride solution was used for the quantitative separation of cuprous oxide from cupric oxide and the metallic copper, while a dilute solution of sulfuric acid was used for the separation of cupric oxide from metallic copper. The metallic copper is dissolved in nitric acid. After separation of the mixture into its components the copper is determined by iodometric, electogravimetric, and permanganate methods.

The results in Table 1 show that metallic copper is practically insoluble in ammonium chloride and only an insignificant amount of cupric oxide is dissolved. The cupric copper which does go into solution forms a complex ion, the reaction of which with metallic copper is considerably weakened. If the reaction is carried out in an atmosphere of CO_2 and oxygen-free solutions are used the cuprous oxide is not oxidized to the bivalent state and the metallic copper does not dissolve. The cupric copper which goes into solution does not interfere with the determination

TABLE 1

Solubility of Copper Compounds in 15% Ammonium Chloride Solution. An aliquot is treated with ammonium chloride for 5 minutes while heating to 100° in a stream of CO_2. The amount of copper which enters solution is determined iodometrically.

Experiment No.	Weight of sample, in g			Amount of NH_4Cl, in ml	Amount of the copper compound which goes into solution
	Metallic	Cuprous	Cupric		
1	0.1000	-	-	15	0.0000
2	0.1000	-	-	15	0.0000
3	-	-	0.1000	15	0.0002
4	-	-	0.1000	15	0.0002
5	-	0.1000	-	15	0.0999
6	-	0.1000	-	15	0.0999

of the cuprous oxide, particularly in the permanganate method. Dilute sulfuric acid readily dissolves cupric oxide, partially dissolves cuproud oxide, but does not dissolve metallic copper to any extent.

Preliminary Investigations.

Initially experiments were carried out on metallic copper with each of the oxides in turn. Afterwards metallic copper was determined together with one of the oxides in the presence of the other oxide (only one of the components was determined in the mixture, assuming the presence of the other but not quantitatively evaluating it). Finally all the components were determined in the mixture of cupric and cuprous oxides and metallic copper.

Cuprous oxide was determined as follows. A sample was treated with 1 N ammonium chloride. In order to accelerate the rate of solution the solution was heated almost up to the boil. The solution obtained of the complex compound of univalent copper was diluted with water, acidified with sulfuric acid and titrated with 0.1 N potassium permanganate[1]. Potassium iodide was thenadded to the solution and the iodine liberated titrated with 0.1 N sodium thiosulfate[2] using starch as an indicator. In this way the cuprous oxide is first determined by permanganate and then by a iodometric method.

From this it appears that 1) cuprous oxide dissolves only very slowly in 1 N ammonium chloride, and 2) the permanganate method gives much lower results than the iodometric one, which gives the correct results. On the basis of systematic analysis it was established that in order to increase the rate of solution it is better to use an ammonium chloride solution with a concentration of not less than 15%.

In order to prevent oxidation of the univalent copper by aerial oxygen which can affect the results considerably, the cuprous oxide should be dissolved, and all further operations conducted in an atmosphere of CO_2, using solutions from which all the air has been expelled by prolonged bubbling of CO_2 through the solutions.

Cuprous oxide is thus determined in the presence of metallic copper and cupric oxide. The solution of cuprous oxide in ammonium chloride is filtered from the cupric oxide and metallic copper and the copper in solution determined by the permanganate and iodometric methods. Results are given in Table 2.

---

1) Initially the titration with permanganate was carried out after addition of a solution of ferric chloride [3], but this practice was discontinued since addition of $FeCl_3$ proved to be unecessary.

2) Excess permanganate is removed by addition of one or two drops of sodium oxalate.

Cupric oxide is determined iodometrically after dissolving the cupric oxide in sulfuric acid, by titration with 0.1 N sodium thiosulfate. In those cases where the cupric oxide is mixed with metallic copper and cuprous oxide, the latter is preliminarily removed by ammonium chloride solution. The residue, consisting of cupric oxide and metallic copper, is then worked up with dilute sulfuric acid. The solution obtained is diluted with water, filtered from metallic copper, and the copper in solution determined iodometrically or by the method of internal electrolysis. Results are given in Table 3.

TABLE 2

Determination of copper as cuprous oxide by the permanganate and iodometric methods

The sample is dissolved in 15% ammonium chloride. Sulfuric acid is added to the solution thus obtained, and the copper is determined by the permanganate method and then by the iodometric method

Experiment No.	Weight of cuprous oxide sample, in g	Vol. of 0.1254 N $KMnO_4$ used, in ml	Vol. of 0.0963 N $Na_2S_2O_3$ used, ml	Amount of copper, g		Difference	
				Found	Actual	Absolute, in g	Relative, in %
1	0.1000	-	14.47	0.0886	0.0888	-0.0002	0.23[4]
2	0.1000	10.10	-	0.0805	0.0888	-0.0083	9.35
		-	14.50	0.0888	0.0888	-0.0000	0.00
3	0.1000	9.00	-	0.0717	0.0888	-0.0171	19.23[2]
		-	14.35	0.0878	0.0888	-0.0010	1.01
4	0.1000	10.40	-	0.0829	0.0888	-0.0059	6.74[3]
		-	14.50	0.0888	0.0888	-0.0000	0.00
5	0.1000	10.50	-	0.0837	0.0888	-0.0051	5.77[3]
		-	14.37	0.0879	0.0888	-0.0009	1.04
6	0.1000	9.10	-	0.0725	0.0888	-0.0163	18.35[4]
		-	14.40	0.0881	0.0888	-0.0007	0.79

1) Sample dissolved with warming in 15% ammonium chloride without CO_2.
2) Sample dissolved in the cold without CO_2.
3) Solution and titration of the cuprous oxide carried out in CO_2.
4) Sample dissolved in the absence of CO_2. Before titration a solution of ferric chloride was added.

TABLE 3

Determination of copper as cupric oxide by electrolytic and iodometric methods. The sample of cupric oxide is dissolved in sulfuric acid (1:3), and the copper in solution determined electrolytically and iodometrically.

Expt. No.	Weight of cupric oxide sample, g	Vol. of 0.0963 N $Na_2S_2O_3$ used, ml	Amount of copper, in g		Difference		Observation
			Found	Actual	Absolute, g	Relative %	
1	0.1000	13.02	0.0797	0.0799	-0.0002	0.24	Cuprous oxide removed with 15% ammonium chloride and metallic copper filtered off after dissolving cupric oxide in H_2SO_4
2	0.1000	13.08	0.0798	0.0799	-0.0001	0.15	
3	0.1000[1]	13.00	0.0796	0.0799	-0.0003	0.40	
4	0.1000[1]	13.05	0.0799	0.0799	+0.0000	0.00	
5	0.1000[1]	13.08	0.0800	0.0799	+0.0001	0.11	

1) The cupric oxide samples contain 0.1 g each of cuprous oxide and metallic copper as well as cupric oxide.

Metallic copper was determined iodometrically after dissolving it in acid. The sample of pure copper was dissolved in nitric acid (1:1) or in concentrated sulfuric acid with heating. When metallic copper is mixed with cuprous and cupric oxides, the cuprous oxide is first removed by dissolving it out with ammonium chloride, then the cupric oxide is removed with dilute sulfuric acid and the metallic copper left determined by the method described above.

Since it is necessary to filter twice and the presence of the filter interferes with the determination of the end point of the titration during iodometric titration, the last filter with its precipitate is dried and ignited in a porcelain crucible. Results are given in Table 4.

When it is necessary to determine all three components in the mixture the procedure is as follows: The cuprous oxide is removed by dissolving it out with ammonium chloride, the residue is extracted with dilute sulfuric acid to remove the cupric oxide, while the metallic copper which remains is dissolved in concentrated nitric or sulfuric acids. The copper is then determined iodometrically in all three solutions, in addition the cuprous oxide is determined by the permanganate method.

TABLE 4

Determination of Copper in Metallic Copper Electrolytically and Iodometrically.

The sample of electrolytic copper is dissolved in nitric acid; the solution is evaporated to dryness; the residue is dissolved in sulfuric acid and the solution formed diluted with water. The copper is determined electrolytically and iodometrically.

No. of expt.	Amount of sample of metallic copper, in g	Vol. of 0.0963 N $Na_2S_2O_3$ used, in ml	Amount of copper in, g		Difference		Observation
			Found exptl.	Actual	Absol.	Relative (%)	
1	0.1000	16.35	0.1001	0.1000	+0.0001	0.10	Cuprous oxide removed with ammonium chloride and cupric oxide with sulfuric acid
2	0.1000	16.33	0.1000	0.1000	0.0000	0.00	
3	0.1000[1]	16.45	0.1007	0.1000	+0.0007	0.70	
4	0.1000[1]	16.25	0.0995	0.1000	-0.0005	0.50	

[1] The samples of metallic copper contain 0.1 g of cuprous and cupric oxides.

In the titration of copper with permanganate a standard solution of manganese sulfate is added to counteract the interference of the Cl' ions. The normality of the permanganate solution was determined with sodium oxalate in the presence of ammonium chloride.

As a result of these preliminary tests the folowing analytical procedure was worked out for the analysis of mixtures of cuprous oxide, cupric oxide and metallic copper.

The test mixture, which contained 0.1 g each of metallic copper, cuprous oxide and cupric oxide, was weighed out into a 100-200 ml dry conical flask and all the air expelled by passing CO_2. 10-15 ml of 15% ammonium chloride solution is added. The solution is heated until all the cuprous oxide is dissolved, 2-3 minutes are usually enough (until all the red particles disappear). The solution is then filtered in a stream of CO_2, the solution diluted to 40 ml with water, and 10-15 ml of 1 N sulfuric acid added. The cold solution is then titrated with potassium permaganate until a faint rose color is obtained, which persists for 2 minutes. A blank is performed at the same time.

The excess permanganate is reduced with a solution of sodium oxalate. 2-3 g of potassium iodide is added to the colorless solution and the iodine liberated is titrated with 0.1 N sodium thiosulfate, using starch as an indicator. From the amount of potassium permanganate and sodium thiosulfate used the amount of cuprous oxide can be calculated from the formula:

$$P_{Cu} = K \cdot V \cdot 0.06354, \qquad (1)$$

where P_{Cu} is the amount of copper as cuprous oxide; K is the normality of the solution; V is the volume of the titrant; and 0.06354 is the milliequivalent of copper.

The filter and residue of metallic copper and cupric oxide are transferred to a 50-100 ml conical flask and worked up with 10-15 ml of dilute sulfuric acid (1:3). The solution of cupric sulfate formed is filtered and the filter washed 3-4 times with water, the filtrate then being diluted to 50 ml and the copper determined iodometrically. The amount of cupric oxide can be calculated from Formula (1).

TABLE 5

Determination of copper in a mixture of cuprous oxide, cupric oxide, and metallic copper

The sample, which consists of cuprous oxide, cupric oxide, and metallic copper, is treated successively with 15% ammonium chloride solution with heating in a stream of CO_2, dilute sulfuric acid (1:3), and nitric acid (1:1). The solutions obtained are analyzed separately for their copper contents.

Expt. No.	Amount of copper sample, in g			Vol. of 0.1254 N $KMnO_4$ used, ml	Vol. of 0.0963 N $Na_2S_2O_3$ used, ml	Amount of copper, in g		Difference	
	Metallic	Cupric	Cuprous			Found	Actual	Absolute (g)	Relative %
1	0.1000	–	–	–	16.21	0.0992	0.1000	-0.0008	0.80
	–	0.1000	–	–	13.05	0.0799	0.0799	0.0000	0.00
	–	–	0.1000	10.80	–	0.0862	0.0888	-0.002	2.96
	–	–	–		14.60	0.0900	0.0888	+0.0012	35
2	0.1000	–	–	–	16.20	0.0992	0.1000	-0.0008	0.80
	–	0.1000	–	–	12.75	0.0788	0.0799	-0.0011	1.37
	–	–	0.1000	10.90	–	0.0869	0.0888	-0.0019	2.16
					14.50	0.0888	0.0888	0.0000	0.00
3	0.1000	–	–	–	–	–	–	–	–
	–	0.1000	–	–	12.80	0.0784	0.0799	-0.0015	1.93
	–		0.1000	11.00	–	0.0877	0.0888	-0.0011	1.15
			–	–	14.05	0.0888	0.0888	0.0000	0.00
4	0.1000	–	–	–	15.75	0.0904	0.1000	-0.0036	3.54
	–		0.1000	9.8	–	0.0781	0.0888	-0.0107	12.10
				–	14.50	0.0888	0.0888	0.0000	0.00

The residue of metallic copper and the filter itself are removed to a porcelain crucible in which they are dried, ignited, and calcined. The calcined residue is finally dissolved in sulfuric acid. The copper is determined iodometrically. The results given in Table 5 show that our method gives satisfactory results. The difference between individual determinations lies within the limits of the permissible error.

Determination of Copper in Copper Powders

The method described above was used for the analysis of copper powders, the results for which are given in Table 6. In order to compare the results obtained by the method described and those obtained by other methods, a series of determinations of the copper oxides and metallic copper was carried out using Lavrukhina's method [2]. Results by the different methods are compared in Table 7. Table 7 shows that results by Lavrukhina's method are in good agreement with those obtained by our method.

SUMMARY

1. A rapid method has been worked out for the determination of cupric oxide, cuprous oxide, and metallic copper in mechanical mixtures of all three.

2. Cuprous oxide can be determined with an accuracy up to 1% by the iodometric method and up to 2-3% by the permanganate method. The cupric oxide and metallic copper can be determined with an accuracy of up to 1% (relative).

TABLE 6

Determination of cuprous oxide, cupric oxide and metallic copper in copper powders. The determinations were carried out by the method described

No. of expt.	Amount of copper powder, in g	Copper found, in g			Observation
		Metallic	Cuprous	Cupric	
1	0.5000	0.3220	0.0010	0.1780	The cupric and cuprous oxides are calculated as cupric and cuprous respectively.
	0.5000	0.3200	0.0010	0.1720	
2	0.5000	0.3330	0.0040	0.1630	
	0.5000	0.3300	0.0040	0.1600	
3	0.5000	0.3500	0.0020	0.1420	
	0.5000	0.3450	0.0020	0.1420	
4	0.5000	0.3900	0.0010	0.1000	
	0.5000	0.3900	0.0010	0.1000	
5	0.2000	0.1700	0.0020	0.0290	
	0.2000	0.1700	0.0010	0.0300	
6	0.5000	0.4840	–	0.0050	
	0.5000	–	–	–	

TABLE 7

Comparison of results of copper powders obtained by our method and Lavrukhina's method.

No. of expt.	Designation of sample	Wt. of sample in g	Copper found, in g (Lavrukhina's method)			Copper found, in g (Our method)		
			Metallic	Cuprous	Cupric	Metallic	Cuprous	Cupric
1	Copper powder No. 1	0.5000	0.3220	0.0010	0.1780	0.3200	0.0010	0.1780
2	Copper powder No. 2	0.5000	0.3330	0.0040	0.1630	0.3320	0.0030	0.1630
3	Copper powder No. 3	0.5000	0.3420	0.0020	0.1400	0.3500	0.0020	0.1420
4	Copper powder No. 4	0.5000	0.3820	0.0030	0.1000	0.3900	Traces	0.0900
5	Copper powder No. 5	0.2000	0.1600	0.0010	0.0300	0.1700	0.0015	0.0290
6	Copper powder No. 6	0.3000	0.2700	Traces	0.0380	0.2600	Traces	0.0380

3. Determination of cuprous oxide, cupric oxide and metallic copper can all be done on one sample.

4. One hour is sufficient for a complete analysis.

5. The main advantage of the method is its simplicity.

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THE USE OF MORPHOLINE IN ANALYTICAL CHEMISTRY

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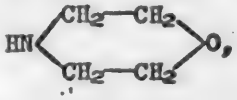
Morpholine C_4H_9NO, or tetrahydro-1,4-oxazine



is a colorless, oily, volatile liquid which has a characteristic amine odor. It dissolves readily in water, alcohol and ether; its melting point is 128.9°; its hardening point 4.9; its specific gravity 0.99; it burns with a bluish flame.

In its chemical properties morpholine is a weaker base than ammonia. It forms easily crystallizable salts with acids and precipitates many heavy metal salts from their aqueous solutions mainly as the hydrated oxides or basic salts.

There is practically no information of the use of morpholine in analytical chemistry in the literature.

We have shown the possibility of using morpholine in qualitative analysis as a reagent for the identification of bismuth and cadmium ions.

Detection of Bismuth with Morpholine in the Presence of Potassium Iodide

One of the characteristic reactions for bismuth is the formation of crystalline precipitates of complex salts of a red, yellow or orange color on the addition of potassium iodide and organic bases. We studied this reaction using morpholine as the base and found that morpholine gives an orange-red precipitate with bismuth salts in the presence of potassium iodide in a nitric acid solution. Under the microscope the crystals appear as rhombs, tetragons and hexagons. The precipitate is insoluble in alcohol, soluble in hydrochloric acid and excess potassium iodide, but decomposes on treating with water or alkalis.

It was observed that on addition of 10% potassium iodide solution dropwise to a nitric acidified solution of a bismuth salt containing morpholine in a test tube, the sensitivity of the reaction corresponds to a limiting concentration of bismuth of 1:4400.

The sensitivity of the reaction can be considerably increased if it is carried out as follows; 2-3 ml of bismuth nitrate is placed in a test tube and the morpholine added. A white precipitate of bismuth hydroxide is formed; at low concentrations the precipitate is practically imperceptible nevertheless the solution is filtered through a filter paper. The filter paper is then unfolded and a drop of nitric acid placed (1:10) on its center. This spot is touched with a capillary tube containing a 10% solution of potassium iodide. An orange red precipitate is formed. This method gives a clear cut result at a concentration of 1:50,000 of bismuth. At concentrations of 1:100,000 an indistinct reddish coloration is produced.

This reaction is very suitable for the detection of traces of bismuth in a solution containing large amounts of copper and cadmium while carrying out the normal systematic qualitative analysis (in the sub-group copper, bismuth, and cadmium).

Method of identification. Morpholine is added to the test solution until an alkaline reaction is obtained; at this point copper, cadmium, and bismuth are precipitated as hydroxides. To the solution ammonium nitrate is added. The precipitate of the hydroxides of copper and cadmium dissolves with the formation of ammoniates, while the bismuth hydroxide is filtered (even though at low concentrations of bismuth it seems to be clear), and the filter paper washed. The filter paper is then unfolded, moistened with morpholine, and a drop of nitric acid placed on the center; this point is touched with a capillary containing 10% potassium iodide. An orange-red color indicates the presence of bismuth.

A Microcrystalloscopic Reaction for Cadmium Based on the Formation of Cadmium Morpholinethiocyanate

The capacity of cadmium to give slightly soluble, complex salts with a characteristic crystalline form with organic bases and ammonium thiocyanate has found application in the microcrystalloscopic detection of cadmium. We studied this reaction using morpholine as the base.

It was observed that a few minutes after the addition of a solution of morpholine and potassium or ammonium thiocyanate to a solution of a cadmium salt, a coarse, colorless crystalline precipitate of cadmium morpholinethiocyanate is formed. The rate of formation depends on the concentration and can be increased by rubbing the sides of the test tube with a glass rod. This precipitate is soluble in excess ammonium thiocyanate (but not in excess potassium thiocyanate), and readily dissolves in acetic and mineral acids; on shaking up with a large volume of water it hydrolyzes with the formation of white flocs of cadmium hydroxide. The precipitate only settles out on long standing from very dilute solutions.

For microcrystalloscopic detection the procedure adopted is as follows. A drop of test solution is placed on a glass slide and a drop of 20-30% solution of morpholine added, together with a crystal of potassium thiocyanate. On standing, or on rubbing with a glass rod, a crystalline precipitate is formed, which is then examined under the microscope. Pure morpholine or concentrated solutions of it should not be used for the reaction, since morpholine forms a salt with potassiumthiocyanate, which on rubbing with a glass rod separates out as colorless crystals in the form of trapeziums, reactangles and hexagons, needles, etc. 20-30% morpholine does not form crystals with potassium thiocyante.

It was found that on addition of a crystal of potassium thiocyanate to a mixture of a drop of a solution of cadmium salt and a drop of 20-30% morpholine, colorless crystals of cadmium morpholinethiocyanate are formed as parallellograms, rhombs, and crystals of other characteristic shapes (Figs. 1, 2, and 3.– see Plate page 359). In moderately dilute solutions of cadmium salts, the precipitates which are formed by friction with a glass rod have a more characteristic form, although the crystals are smaller; in very dilute solutions, single characteristic crystals are formed after several minutes. The limit of identification is 0.1 μg of cadmium. The limiting concentration is 1:10,000. The sensitivity of this reaction is higher than that of similar reactions with other organic bases.

In addition to cadmium, zinc, lead, mercury and copper and moderately concentrated solutions of nickel give crystalline precipitates under the conditions indicated above. If both cadmium and copper are present, greenish-yellow crystals are formed, probably of the mixed salt.

The author wishes to express her thanks to I.P.Ryazanova for permission to carry out this work in the Saratov University laboratory, and to V.A.Voshchin for preparing the microphotographs of cadmium morpholinethiocyanate.

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Fig. 1. Crystals of cadmium morpholine-thiocyanate from Cd^{2+} solutions of concentration 1:5000 (magnification 120).

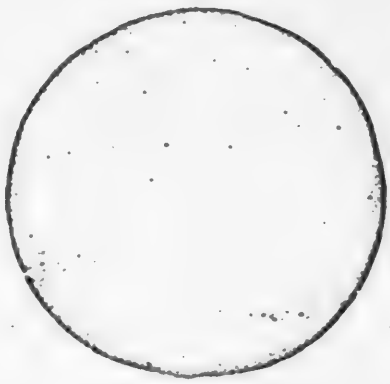

Fig. 2. Crystals of cadmium m morpholinethiocyanate from Cd^{2+} solutions of concentration 1:1000 (magnification 120).

Fig. 3. Crystals of cadmium morpholinethiocyanate from Cd^{2+} solutions of concentration 1:200 (magnification 120).

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DETERMINATION OF SMALL AMOUNTS OF NITROGEN IN GASES

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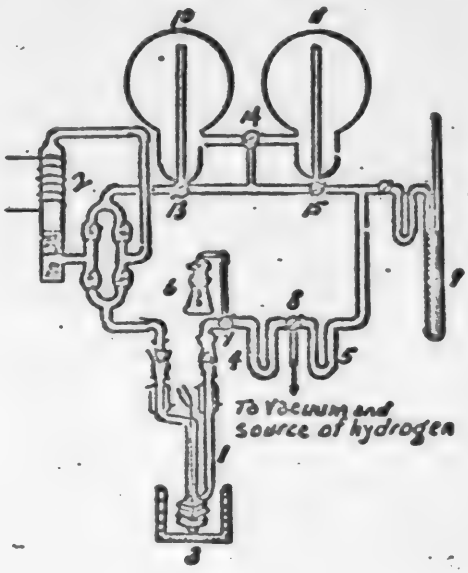
Hydrogen and other gases often contain small amounts of nitrogen. By means of the method described below it is possible to determine nitrogen directly in gaseous mixtures. In its simplest form the method can be applied to the determination of traces of nitrogen in hydrogen.

The hydrogen which contains nitrogen is circulated several times through a closed system containing a catalyst for converting the nitrogen into ammonia and a trap cooled with liquid air until all the nitrogen has been removed as ammonia. The amount of ammonia formed is then determined by the usual methods.



The apparatus is shown schematically in the diagram. The total volume of the apparatus as used in our experiments could be varied from 1-10 liters (the volume is changed by including or excluding supplementary flasks 10 and 11 by means of the taps 13, 14 and 15). The gas is circulated by means of a glass electromagnetic pump 2 [1]. Flask 1 made of pyrex contains 30 g of the catalyst for ammonia synthesis in the form of grains 2-3 mm in diameter. The catalyst is reduced at the

begining of an experiment. The vessel is provided with a coil for preliminary heating of the gas. The gas is heated by means of an electric furnace 3. The temperature of the catalyst is measured with a thermocouple. Experiments are conducted at 475°. Circulation of the gas mixture is continued until the ammonia which is frozen in the tube 4 filled with broken glass ceases to be formed. For a content of 1% of nitrogen in the test gas a few hours is necessary for complete conversion into ammonia at a circulating rate of 300-500 liters per hour. In order to check that all the nitrogen has been converted into ammonia, U tube 5 which precedes tube 4 is periodically cooled with liquid air. The absence of any deposit of solid ammonia in this tube indicates the end of the reaction. The trap 4 is then allowed to warm up to room temperature and the ammonia blown by a stream of hydrogen through tap 8 into flask 6 containing standard sulfuric acid. Excess acid is then back-titrated with NaOH using a microburet. Before intake of a new sample the apparatus is evacuated[1]. By means of this method nitrogen can be determined in hydrogen at a concentration of $1 \cdot 10^{-3}$% vol. with a possible error of $\pm 5 \cdot 10^{-5}$.

The method can also be used for the determination of small amounts of nitrogen in various gases such as argon or other inert gases[2]. A small amount of nitrogen-free hydrogen must be added to other gases containing nitrogen before carrying out the procedure described above.

The method can also be used for freeing hydrogen from contamination with nitrogen. Hydrogen cylinders usually contain up to 1% nitrogen. It could also be used for removing nitrogen from inert gases. E.g. if it is required to determine nitrogen in argon using hydrogen from a cylinder, the hydrogen is allowed into the system up to a pressure of 1/2 atmosphere. The nitrogen in the hydrogen is converted into ammonia which is frozen in trap 4. After disconnecting tap 4 from the system by means of taps 7 and 8 the ammonia is removed by pumping out in a frozen state under high vaccuum. The gas to be analyzed is then led into the system, the amount introduced being found by the increase in pressure measured by manometer 9 (the volume of the system should be known). The determination is then carried out as described above. The hydrogen used for combining with the nitrogen can be removed by heated cupric oxide.

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Received November 23, 1951

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1) Air must be excluded from the apparatus since this will lead to deterioration of the catalyst

2) I.P.Krichevsky pointed this out.

AN APPARATUS FOR THE DETERMINATION OF NITROGEN IN GASESOUS MIXTURES

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Up to the present it has been current practice in gas analysis to assume that the gaseous residue which cannot be determined by the use of the normal absorbents or by fractional combustion, is nitrogen. This residue is determined at the end of the determination by difference. Such a method inevitably leads to a lower accuracy since all the errors in the individual determinations add up in the residue. In view of the fact that a direct determination of nitrogen is necessary for many investigations, various methods have been proposed during the last 50 years which to some extent answered the purpose for a particular problem.

Lidov [1] studied the absorption of nitrogen by metallic magnesium and mixtures of magnesium and calcium as far back as 1902 and on this basis proposed a method for the determination of nitrogen in its mixtures with other gases and in chemical compounds. His apparatus and technique have been simplified by Blumstein [2]. Henrich and Eichorn [3] described an apparatus in which the nitrogen is ignited by means of an electric discharge in the presence of hydrogen. Fisher and Ring [4] used calcium carbide for binding the nitrogen.

Dementeva [5] for the determination of nitrogen in gases recommended a special apparatus in which all the gases are ignited to CO_2 and H_2O. CO_2 is absorbed and the gas left is assumed to be nitrogen.

All the apparatuses described above however are of complicated construction and consequently they are expensive and are difficult to control.

In 1950-1951 we constructed a simpler and more portable apparatus than the rather cumbersome appartus which have been proposed previously and which are rarely used in practice.

Description of Apparatus

The apparatus consists of the following major parts (See diagram). A measuring buret of 5-10 ml capacity fitted with a three-way tap 1 and a levelling tube with a tap 3 are fixed on a glass frame provided with two leads (inlet and outlet for water to maintain the temperature constant during an analysis) and a thermometer.

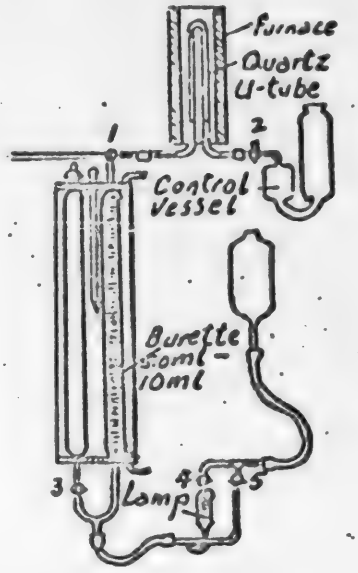
A pear-shaped vessel containing mercury is connected through a rubber tube with a lamp in the form of a cylinder. The additional tube with two taps 4 and 5 serves as a regulator for the velocity with which the gas is removed from the buret into U-tube. A control vessel with a three way tap 2 which acts as a receiver for excess gas not absorbed on passing through the U-tube. An electric furnace working at 800-900°. A quartz U-tube.

Preparation of the Apparatus for Analysis

Clean mercury is poured into the levelling pear shaped vessel, tap 5 is opened and the connecting rubber tube and all the glass connections filled, care

1) Student V.P.Bogdashev participated in this work.

being taken to exclude any bubbles of air. In this way all the measuring buret is filled with mercury. During this operation the buret is open to the atmosphere via tap 1. Taps 2, 3 and 4 are closed. When all the measuring buret is filled with mercury (right up to the zero mark) tap 5 is closed again.



The U-tube is then swept out with any inert gas or hydrogen which are free from any contaminations. The U-tube is a bent quartz tube (height 8-10 cm and internal diameter of 4-5 mm) filled with powdered metallic magnesium (2-3 g). The U-tube has an internal diameter of 5 mm and an external diameter of 7 mm. The bent back ends of the U-tube are made in the form of capillaries with external diameter 7 mm and internal diameters of 1 mm and 2 mm on different sides. The magnesium is sieved beforehand through a 40 mesh sieve (40 openings/cm^2) washed thoroughly with carbon tetrachloride and dried.

In order to fill the U-tube with magnesium in the least possible time in one operation we suggest the following procedure: the end of the U-tube connected to the smaller capillary is covered with a wad of cotton wool and pressed against a vaccuum lead, while the other end is placed in the box containing the metallic magnesium. By moving the end of the U-tube about continuously in the box containing the powder the U-tube can be filled in about 1-2 minutes.

Before a run it is essential to calcine the U-tube with hydrogen in a crucible or muffle furnace for one hour at 800° in order to remove any gases adsorbed by magnesium (mainly hydrogen). If argon is being used there is no need to calcine.

Although magnesium on its own absorbs nitrogen much slower than when it is mixed with calcium oxide and metallic sodium and considerably slower than metallic calcium on its own, nevertheless possible errors arising from the presence of hydrogen or methane etc. in the test gas are excluded.

Metallic calcium is known to absorb hydrogen actively forming calcium hydride, while if calcium oxide is used there is a possibility of a reaction between it and any hydrocarbons at the expense of the oxygen of the CaO.

Argon or hydrogen is passed through the leading-in capillary, tap 1, U-tube and through tap 2 open to the atmosphere. Tap 2 is then closed so that the U-tube is completely sealed off (tap 1 is also switched to exclude the atmosphere) and the control vessel opened to the atmosphere.

Analytical Procedure

After the apparatus has been prepared for analysis as described above, the test mixture of gases (residue after absorption of CO_2; C_nH_{2n}; O_2 and CO by the usual methods of gas analysis) is sucked through the inlet capillary and tap 1 (open to the atmosphere) into the measuring buret. In order to do this the levelling pear-shaped vessel is lowered and the gas intake regulated by means of tap 5. When the intake of gas for analysis is complete, tap 5 is closed, tap 3 is opened and the gas adjusted to normal pressure (by levelling with the pear shaped vessel until the levels in the measuring buret and the levelling tube coincide) and readings made of the exact volume of gas taken for analysis, the temperature, and the

barometric pressure. The electric furnace is then switched on and when the U-tube has been heated to the requisite temperature (while the U-tube is being heated it is connected via tap 2 with the control vessel for egress of the expanding hydrogen or argon) the test gas is allowed to pass through it.

The measuring buret is connected with the U-tube via tap 1, and on opening tap 2, tap 4 is also slowly closed so that the mercury, with the requisite velocity, gradually flows through the capillary branch. The mercury which flows out drives the gas from the measuring buret into the U-tube. The gas which passes through the heated metallic magnesium proceeds to the control vessel. In this case the operation of circulating the gas through the U-tube must be repeated, the gas being led back from the control vessel into the measuring buret (the flow rate of the gas is 2-3 ml/minute).

In order to carry out the recirculation tap 4 is closed and tap 5 is opened and with taps 1 and 2 also opened the pear-shaped vessel with the mercury lowered. When this is done the gas from the control vessel quickly passes through the U-tube into the measuring buret (because of the vaccuum created by the mercury flowing rapidly from the measuring buret, through tap 5 and the additional tube into the pear shaped bulb which has been lowered). The transfer is continued until the mercury from the control vessel is sealed off by the capillary at tap 2. The gas is repeatedly passed through the U-tube until the volume of the residual mixture remains a constant. The nitrogen content of the test mixture is then calculated from the difference in volume of gas before and after circulation through the system. The volume is measured after the U-tube has cooled. When this is done, part of the gas is transferred from the buret into the vessel in order to avoid formation of a vacuum. All the apparatus is mounted in a small box (of the same type as the Ors apparatus). A drip pan should be fitted under the apparatus to catch any mercury which might spill.

An evaluation of the accuracy of the determination of nitrogen by means of this apparatus may be made on the basis of the following considerations. Analytical error during the process of absorbing nitrogen can arise from insufficient removal of excess hydrogen during saturation of the magnesium (calcining at 800° for 1 hour before analysis) or from the presence of oxygen-containing compounds in the hydrogen used. At, 800°, oxygen, CO_2, etc. react with hydrogen and saturated hydrocarbons so that the final volume of the mixture is changed. This must always be taken into account.

Usually for a measuring buret of 5 ml capacity graduated to 0.05 ml, readings can be taken with an accuracy of 0.02-0.025 ml. Consequently for such an accuracy the absolute error of the apparatus is equal to 0.02-0.025 ml and the relative error in this case (assuming a total volume of 5 ml) will be 0.5%.

Since it is more expedient to determine the nitrogen after absorption of CO_2, unsaturated hydrogen, O_2 and CO i.e. to determine it from the remaining mixture of gases consisting usually of hydrogen, saturated hydrocarbons and nitrogen, then the value of the relative error with respect to the total residue increases somewhat.

But if it is taken into account that the hydrogen and saturated hydrocarbons in another sample of the test mixture are determined by combustion with an accuracy of up to 0.2-0.3%, then on comparing the result of both analysis (for nitrogen on the one hand and hydrogen and saturated hydrocarbons on the other) the maximum error as shown experimentally amounts to 1% i.e. within the limits of the errors of normal gas analysis.

SUMMARY

We have designed an apparatus which is based on a chemical method for the determination of nitrogen indicated by A.P.Lidov. The analytical technique for the analysis of mixtures left after the usual absorptions is more simple, and the

apparatus designed in such a way that it is incomparably more portable than apparatus suggested previously (which have accordingly not been widely adopted) and can be made in any laboratory.

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CHRONICLE

FROM THE CHEMICAL SCIENCES SECTION OF THE ACADEMY OF SCIENCES U.S.S.R.

The Commission on the History of Chemistry from the Chemical Sciences Section of the Academy of Sciences USSR has started preparations for convening a Third All-Union Conference on the History of Chemistry which it proposes to hold during 1953.

The chief purpose of the future conference will be the consideration of basic questions connected with the preparation of a text book on the History of Russian Chemistry and monographs on the most important problems in the history of Russian chemistry.

The reports to the conference will be devoted to the following problems:

1. General and methodological problems in the history of chemistry. (Objects, methods, problems, significance of the history of chemistry. The problem of the periodization of the general history of chemistry, periodization of the history of the development of individual branches and divisions of chemistry, periodization of the history of Russian chemistry. Sources of the study of the history of chemistry, criticisms of the work of bourgeois historians of science).

2. The most important stages and paths in the development of chemistry. (History of the development of various nodal problems of Russian chemistry in conjunction with its contemporary position and the perspectives of the development of chemistry. History of the most important directions in the development of chemistry in the Socialist epoch).

3. New facts hitherto unknown and not published in the literature on the discoveries of Russian scientists. The priority of important discoveries of Russian scientists.

The Commission invites participation in the work of the conference.

The subjects of reports or communications should be sent not later than November 1st, 1952.

The Commission at the same time wishes to state that apart from the publication of the proceedings of the conference it intends to issue a Symposium on the Proceedings of the Commission in which various reports heard at the meeting will be published in addition to works of a research nature on the history of chemistry carried out in Academic or Non-academic Institutions.

Articles and communications for inclusion in the next issue of the Symposium on the History of Chemistry must be sent not later than Nov. 1st, 1952.

Any enquiries should be addressed to: Moscow, Bolshaya Kaluzhskaya Dom 31, Comissiya Po Istorii Khimii Otdeleniya Khimicheskikh Nauk, Acad. Nauk, USSR.

Commission on the History
of Chemistry.

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